Fire's Black Legacy:
The Fate of Pyrogenic Carbon in Soils across Scales

Dissertation

zur

Erlangung der naturwissenschaftlichen Doktorwürde
(Dr. sc. nat.)

vorgelegt der

Mathematisch-naturwissenschaftlichen Fakultät

der

Universität Zürich

von

Moritz Reisser

aus

Deutschland

Promotionskommission

Prof. Dr. Michael W. I. Schmidt (Vorsitz)

Dr. Samuel Abiven (Leitung der Dissertation)

Prof. Dr. Ross S. Purves

Zürich, 2018

„We've grown used to wonders in this century. It's hard to dazzle us. [...] We've grown used to the idea of space, and perhaps we forget that we've only just begun.
We're still pioneers. [...]
It's all part of the process of exploration and discovery.
It's all part of taking a chance and expanding man's horizons.
The future doesn't belong to the fainthearted;
it belongs to the brave.[...]
Nothing ends here“

Ronald Reagan (after the Challenger Disaster, 1986)

Abstract

Fires affect roughly 4% of the Earth's surface every year. A major part of the carbon (C) involved in this biomass burning is emitted to the atmosphere as CO_2. However, up to 20% of the involved C is converted into pyrogenic carbon (PyC). These thermally altered remnants of biomass have particular and exclusive features. They have a high C content, are very aromatic in their chemical structure and reside in soils much longer than most other organic compounds. Furthermore, PyC may exhibit a set of positive effects on soil properties, like liming, increasing water retention capacity, retention of pollutants or the long-term availability of nutrients. Due to its high residence time in soils, PyC is also proposed as a means for climate change mitigation through its efficient storage of C in soils instead of fast mineralization to the atmosphere as CO_2.

However, knowledge on the global distribution of PyC in soils is scarce and hampered by the disunity in the scientific field regarding quantification methods. There is hardly any information about what drives the decomposition and stabilization of PyC. The influence of PyC on the residual soil organic carbon (SOC) was studied, but only on relatively short timescales and based on point measurements, which cannot be easily integrated to conclusive values. The scope of this thesis was hence to investigate and model the global distribution of natural PyC based on the current literature, examine the drivers of PyC decomposition and stabilization on varying scales and in different ecosystem, compare and test state-of-the art quantification methods, and lastly improving our understanding of the influence of PyC on SOC after years to centuries.

The results showed that PyC forms one of the biggest identifiable organic compound classes in soils with on average 13.7% of SOC, globally. Its content is driven mainly by soil properties (e.g. clay content and pH), climatic variables (e.g. temperature and precipitation) as well as land use, whle fire is difficult to relate to PyC on the global scale, because the available fire data is too coarse and short-term to capture the relation with PyC contents. We found similar correlations also in a more spatially balanced dataset in Switzerland, where soil properties and climate were again main drivers of PyC contents. However, no specific fire data was available there. Interestingly, PyC was decomposing faster in a temperate ecosystem than in tropical or arctic ones, highlighting the complex mechanisms behind the persistence of PyC in soils. Our data furthermore suggests that PyC exhibits an influence on SOC, which is not only much greater in magnitude than previously thought, but also highly variable and could last for decades or even centuries.

The comparison of three quantification methods yielded similar results in two independent studies. Linear relationships could be established, to enable easy calibration of one method to the other.

In combination, the different studies presented in this thesis improved not only our understanding of the drivers of PyC contents, but also on what spatial and temporal scales certain drivers and processes act predominantly. Further, it offers promising perspectives for future research with unified methods, the potential of PyC to form carbon sinks in soils or the interaction of biotic and abiotic processes governing and governed by PyC.

Zusammenfassung

Jedes Jahr wüten Brände auf bis zu 4% der Landfläche unserer Erde. Während der überwiegende Teil der Biomasse dabei als CO_2 in die Atmosphäre abgegeben wird, verbleiben bis zu 20% als verkohlte Feuerrückstände (Kohle; hier nicht zu verwechseln mit Braunkohle o.ä.) auf Vegetation und Boden. Diese Kohle weist einige besondere Eigenschaften auf: einen sehr hohen Kohlenstoff (C) Gehalt, eine aromatische chemische Struktur, sowie Verweilzeiten in Böden, die viel länger sind als die der meisten anderen organischen Substanzen. Zusätzlich kann diese Kohle auch eine reihe weiterer positiver Auswirkungen auf Böden haben, so etwa pH-Wert Erhöhungen, verbesserte Wasserspeicherung oder Rückhaltung von Schadstoffen. Durch seine hohe Verweilzeiten in Böden ist pyrogener C (PyC) ausserdem ein mögliches Mittel im Kampf gegen den Klimawandel, da es C lange im Boden speichert, anstatt dass dieser schnell wieder in die Atmosphäre abgegeben wird.

Das Wissen über die globale Verteilung von PyC in Böden ist allerdings spärlich und erschwert durch die Uneinigkeit der Wissenschaft, was die Methoden zu Quantifizierung von PyC betrifft. Es gibt nur Vermutungen, wodurch der Abbau und die Stabilisierung von PyC hauptsächlich angetrieben werden. Ausserdem gibt es zwar bereits einige Studien zum Einfluss von PyC auf den restlichen C im Boden, jedoch nur über kurze Zeiträume und basierend auf Punktmessungen. Daher ist es das Ziel dieser Doktorarbeit die globale Verteilung von PyC mit Hilfe von Literaturrecherche zu untersuchen und zu modellieren, die Treiber des Abbaus und der Stabilisierung von PyC auf verschiedenen räumlichen und zeitlichen Skalen und Ökosystemen zu prüfen, zwei modernste Methoden zur Quantifizierung zu Vergleichen und letztlich auch den Einfluss von PyC auf den C im Boden genauer zu verstehen.

Die Resultate zeigen, dass PyC mit etwa 13.7% weltweit einen beachtliche Anteil am C des Bodens ausmacht. Hauptsächlich wird diese Konzentration durch Bodeneigenschaften (Tonanteil, pH Wert) und das Klima (Niederschlag und Temperatur) beeinflusst, sowohl auf globaler, wie auch auf kleinerer Skala. Bei Feuer selbst als Antrieb der PyC Produktion konnten keine Korrelationen mit globalen Datensätzen gefunden werden, da diese noch zu schlecht aufgelöst sind und nur die letzten zwei Dekaden abdecken. Interessanterweise konnten wir in einem Feldexperiment aufzeigen, dass PyC schneller in unseren gemässigten Breiten abgebaut wurde, als in den Tropen oder der Arktis, was aufzeigt, wie kompliziert die betreffenden Prozesse sein müssen. Ausserdem konnten wir beobachten, dass der Einfluss von PyC auf C im Boden weit grösser als bisher angenommen und äusserst variabel zu sein scheint. Durch den Vergleich von Quantifizierungstechniken konnten wir Möglichkeiten zur Kalibrierung der benutzten Methoden zueinander aufzeigen.

Durch die Kombination der einzelnen Studien dieser Doktorarbeit, wird unser Verständnis für die Prozesse und Mechanismen des PyC Abbaus und Stabilisierung auf verschiedenen Skalen verbessert. Des Weiteren bieten sie einige vielversprechende Perspektiven für zukünftige Forschungsfragen betreffend der Vereinheitlichung von Quantifizierungsmethoden, dem Potential von PyC in Böden als C Senke zu agieren oder der Interaktion von biotischen und abiotischen Prozessen, welche durch und auf PyC ausgeübt werden.

Table of Contents

List of Figures

List of Tables

Abbreviations

BPCA	benzene polycarboxylic acid (PyC molecular marker)
CTO	chemothermal oxidation (PyC quantification method)
DRIFT	diffuse reflectance infrared Fourier-transformed spectroscopy
fLF	free light fraction (in density fractionation method)
HF	heavy fraction (in density fractionation method)
HyPy	hydrogen pyrolysis (PyC quantification method)
MAP	mean annual precipitation
MAT	mean annual temperature
MRT	mean residence time (here: = turnover time)
NMR	nuclear magnetic resonance
oLF	occluded light fraction (in density fractionation method)
PE	priming effect
PLSR	partial least square regression
PyC	pyrogenic carbon
PyC_{BPCA}	pyrogenic carbon measured by BPCA
PyC_{HyPy}	pyrogenic carbon measured by HyPy
SOC	soil organic carbon
τ_{short}	short-term turnover time
τ_{long}	long-term turnover time

List of Manuscripts

This cumulative thesis comprises four individual manuscripts that have already been published (1+2), or are submitted (3+4) to peer-reviewed scientific journals.

Manuscript 1

Reisser, M., Purves, R. S., Schmidt, M. W. I., and Abiven, S. (2016): Pyrogenic Carbon in Soils: A Literature-Based Inventory and Global Estimations of Its Content in Soil Organic Carbon and Stocks. *Frontiers in Earth Science* 4, 1-14, doi: 10.3389/feart.2016.00080

Contributions: MR and SA conceived the paper structure. MR collected the database. MR, SA, and RP contributed to the data analysis. MR and SA wrote the manuscript and all authors contributed to the writing of the manuscript.

Manuscript 2

Reisser, M., Ascough, P., González-Domínguez, B., Hagedorn, F., Niklaus, P. A., Wacker, L., Abiven, S.: Long lasting influence of pyrogenic carbon on soil organic carbon and drivers of its content in forest soils. Submitted to PLOS One (June 2018).

Contributions: S.A. and M.R. conceived the study. S.A., B.G-D., P.N. and F.H. developed the initial experimental design and provided additional data. L.W. provided the ^{14}C data. M.R. and P.L.A. conducted the laboratory work. S.A., P.L.A and M.R. interpreted the data and all authors contributed to the writing of the manuscript.

Manuscript 3

Cotrufo, F. M., Boot, C., Abiven, S., Foster, E. J., Haddix, M., Reisser, M., Wurster, C. M., Bird, M. I., Schmidt, M. W.I. (2016): Quantification of pyrogenic carbon in the environment: An integration of analytical approaches. *Organic Geochemistry* 100, 42-50, doi: 10.1016/j.orggeochem.2016.07.007

Contribution: MR measured and analysed the samples with DRIFT. MR contributed to the final version oft he manuscript. (No comprehensive author contributions given)

Manuscript 4

Reisser, M., Maestrini, B., Iturrate-Garcia, M., Sylvester Pungga, R. a., Abiven, S.: The wayward decomposition behaviour of Pyrogenic Carbon in soils – pyrogenic carbon and grass degradation and related priming effect in tropical, temperate and arctic ecosystems. In review at: Scientific Reports (June 2018).

Contributions: S.A. and B.M. developed the experimental design. B.M. and M.R. conducted the field campaigns. M.I.G. and R.A.S.P. supported the fieldwork. M.R. collected and analysed the data. M.R., S.A., B.M. and M.I.G interpreted the data. M.R., S.A., B.M. and M.I.G contributed to the writing of the manuscript.

Part A - Synopsis

1 Introduction

"If you wish to make an apple pie from scratch, you must first invent the universe."
Carl Sagan

1.1 Carbon – The Essence of Life

Carbon (C) is an indispensable element for all life on Earth. Together with oxygen, it accounts for the large majority of mass in every organism. As C is often the basis of long, stable and/or very important molecules, one could even say it is the backbone of life. Organic (geo-)chemistry is defined as the studies of molecules, which contain C in them, with very few exceptions (CO_2, CO_3^{2-}, HCO_3^- and pure C). The special role of C for life stems from a series of chemical and physical properties (Lide, 2017), which will not be discussed here in detail.

Pure C exists in nature in two forms: graphite and diamond. Yet, the majority of C in the earth system is either stored in the form of $CaCO_3$, other mineral forms, or in living or dead biomass. Quantitatively only a minor part of C is actually present in the form of CO_2 in the atmosphere.

Another very important feature of C is that it exists as three different atoms with nearly identical chemical properties but with differing masses (isotopes), of which two are stable in nature. ^{12}C consist of 6 protons and 6 neutrons in its nucleus and is with 98.9 % abundance on Earth the most common form of carbon. ^{13}C has one more neutron in the nucleus and makes up about 1.1 % of natural C (International Atomic Energy Agency, IAEA). ^{14}C with 8 protons, however, is only produced through (solar) radiation on ^{14}N (nitrogen) and is extremely rare in the environment. This ^{14}C is also radioactive, meaning it decays over time, while emitting radiation in the process.

1.2 The Global Carbon Cycle

C on the earth surface is always in movement and in transformation between different pools and spheres. This is called the global carbon cycle outlined in Figure 1. All pools are characterised by different absolute stocks and also different residence times of the C. The spreading of agriculture and the burning of fossil fuels has largely altered the C cycle (indicated with red numbers)(Barker, 2007). **Atmospheric stocks of C in the form of CO_2 have risen from around 275 ppm in pre-industrial times to over 400 ppm to date** (Keeling et al.,

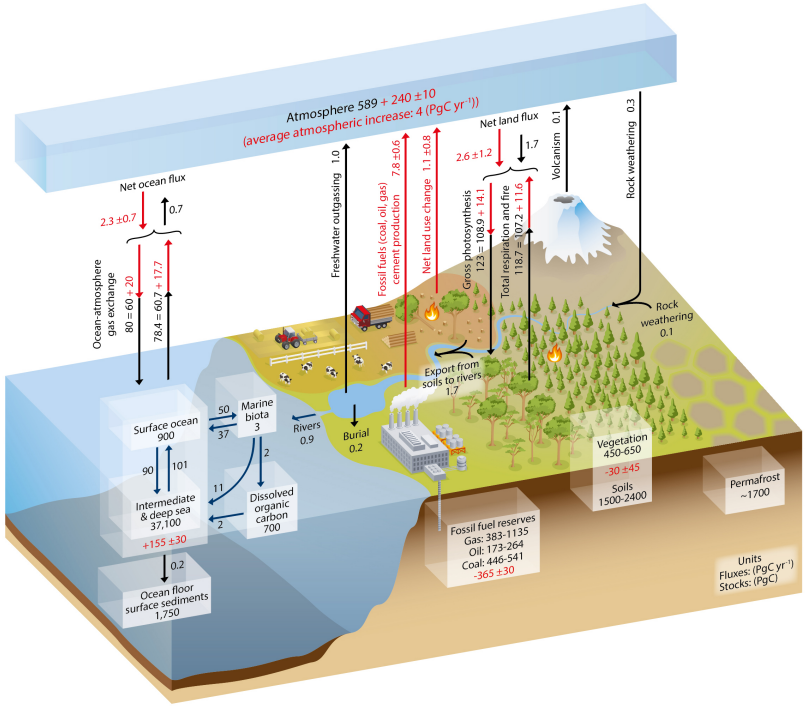


Figure 1: The Global Carbon Cycle. Numbers in the boxes represent stocks, while numbers at the arrows represent fluxes. Red numbers indicate the change since the beginning of industrialization. (IPCC 2013)

2017) corresponding to a current annual increase in the atmospheric stock of 4 Pg of C (IPCC, 2013). This flux seems very small compared to the natural background fluxes, however, even small changes make a great difference over a longer time. This is easily recognizable, by looking at the annual atmospheric increase, compared to other fluxes in the cycle. The number is very small compared to the global uptake of the oceans (~80 Pg), or terrestrial respiration (~120 Pg), yet it still has lead to an increase of atmospheric CO_2 of more than 50 % over the last 150 years. Vice versa a small relative change of a large reservoir can result in a large relative change of a small flux. **For example, a change of the soil stock of only 2-3 ‰, would already be equivalent of the 4 Pg atmospheric increase and could therefore either double it or bring it completely to zero**.

1.3 Carbon's Role in Soils

Soils are the linking elements between aboveground biomass, atmosphere and hydrosphere. **Thus, what happens in soils can have a considerable impact on each of the other spheres**. The relevance of soils as C reservoirs is fostered by the fact, that they store more than double the amount of C than atmosphere and all aboveground biomass together. In fact, a relatively small change in the soil pool

can have large impact on the atmospheric CO_2 level (see example given at the end of the last section), since the main outflux of carbon from the soil happens through mineralization of organic carbon by microbes, respiring it to the atmosphere as CO_2. Therefore we need to understand the dynamics of organic matter and its interactions with the soil and the microbial community. Soil organic carbon (SOC) comprises a great range of different compounds, which enter the soil either as dead biomass or through root exudates. Its content in soils ranges from < 1% to 20 % (FAO/IIASA/ISRIC/ISSCAS/JRC, 2012).

SOC turns in average over on a decadal scale (for an explanation of turnover, turnover time and mean residence time, see figure 2)(Amelung et al., 2008) and we observe a strong correlation with the climate (Carvalhais et al., 2014; Chen et al., 2013; Davidson and Janssens, 2006). However, many more factors have to be considered when looking at the turnover/mean residence time (MRT) of SOC. **Next to the inherent chemical recalcitrance of different organic compounds there is the possibility to physically disconnect SOC from microorganisms in aggregates (Edwards and Bremner, 1967; Lehmann et al., 2007) and to chemically connect to reactive surfaces of minerals**

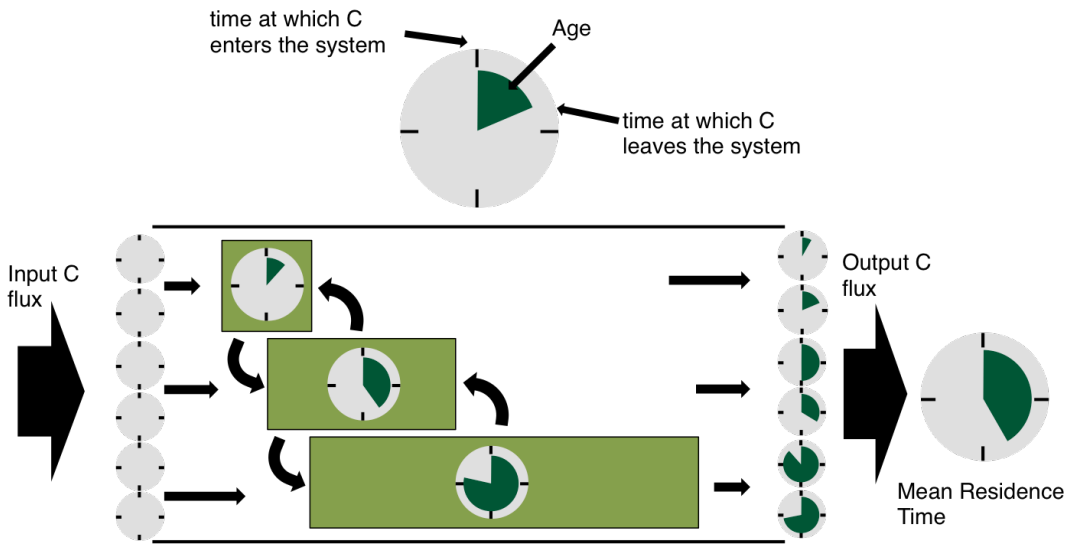


Figure 2: Schematic representation of turnover and MRT at pool and system (soil) level used in this thesis. Usually a system is divided into different pools of differing turnover, indicated in light green here. The average time (turnover time or MRT; here turnover time describes the same as the MRT and can thus be used interchangeably.) that C stays in one of these pools is indicated with the age on the clock in the respective pools as well as the pool's sizes. The MRT of a system is then the mean of the ages, which C spent in the system. Turnover describes here the inverse of the MRT, i.e. how much C travels through the system or a pool in a certain amount of time. There is interaction between different pools and C can change from one to another through different stabilization and de-stabilization processes (e.g. chemical break-down, aggregation or association to minerals). Modified after Sierra et al. (2016).

(Torn et al., 1997). All this can result in a mid- to long-term stabilization of SOC. These processes are again influenced by a set of environmental and ecosystem variables like climate, pH, texture of the soil, vegetation cover or land use. Yet, MRTs of SOC, especially their spatial variability keep being very difficult to predict. While the global MRT of SOC is estimated to average around 50 years, all identifiable compounds in soils per se do have a lower MRT (Amelung et al., 2008; Schmidt et al., 2011) - all, but pyrogenic carbon.

1.4 Pyrogenic Carbon

Pyrogenic carbon (PyC) is the thermally altered remnant of the incomplete combustion of biomass (Goldberg, 1985) when there is not enough oxygen to oxidize all carbon to CO_2. This residue of fire is very rich in carbon and aromatic structures and consists of a continuum of compounds, ranging from slightly charred materials to highly condensed aromatic structures, such as soot (Hedges et al., 2000; Masiello, 2004). **PyC is found in all environments**, be it in the air, water, sediments or soils (Schmidt et al., 2000). It is characterized by a (i) dark colour, (ii) high porosity / low density, resulting in a very high specific surface area and consequently high cation exchange capacity (Lehmann and Joseph, 2015; Liang et al., 2006), (iii) Lower H:C, N:C and O:C ratios than its precursor material (Knicker, 2007), (iv) high recalcitrance to chemical and biological oxidation (Ascough et al., 2011; Santos et al., 2012; Skjemstad et al., 1996) leading to (v) a highly increased MRT compared to

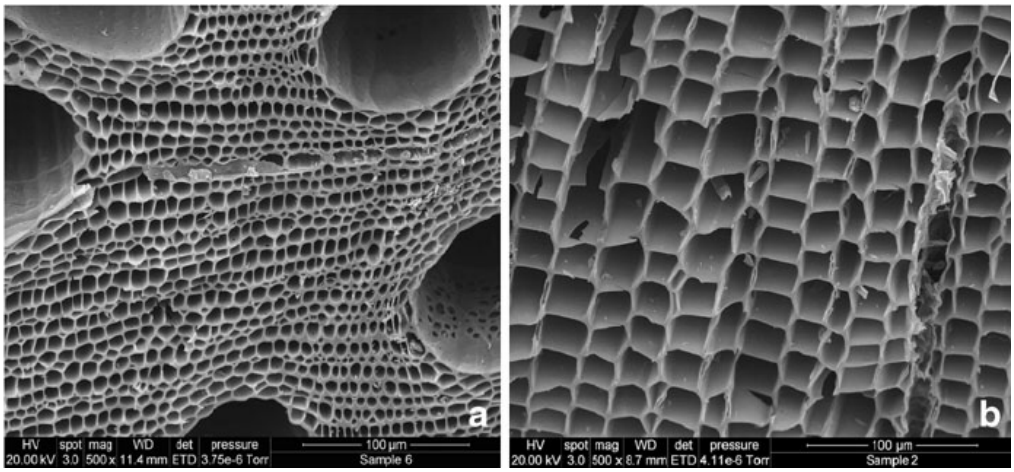


Figure 3: Scanning Electron Microscopy images of PyC a) from eucalyptus bark, and b) from pine wood. The porous structure results from the loss of the cell content, while cell walls are remaining. (Macía and Arbestain, 2010).

its uncharred precursors (Baldock and Smernik, 2002; Zimmerman et al., 2010). The physical structure of PyC is shown in Figure 3.

Due to this set of unique properties, PyC has been proposed to be used as artificially produced soil amendment (biochar) to not only increase soil fertility and sustainability, but also mitigate climate change by storing carbon in the soil on long time-scales (Lehmann, 2007; Lehmann and Joseph, 2015; Macías and Arbestain, 2010). **If PyC would support the increase of global SOC stocks, this could have large impact on the atmospheric CO_2 levels** (see chapter 1.2), adding high and prevailing relevance to the topic. PyC is also very interesting to investigate in its natural forms and ecosystems where it undergoes transformations and pathways similar to C in the global carbon cycle. Additionally, recent studies suggest that **fire frequency is likely going to increase in the coming decades due to the on-going global (climate, land use etc.) change likely leading to a higher production of natural PyC.**

However, whether naturally or artificially produced, PyC is a continuum of different compounds. This has been, and still is posing many challenges to its actual quantification and characterisation. It has been a problem and thus also has been of primary interest for decades to find and improve reliable methods to quantify and characterise PyC (Hammes et al., 2007; Hammes and Abiven, 2013). There is still no globally applied set of accepted characterisation or quantification methods. This thesis contributes to the discussion and improvement of PyC methods, therefore a brief overview on existing methods is given in the next section.

1.5 Quantification and characterisation of Pyrogenic Carbon

The difficulty of reliably quantifying PyC lies in its intrinsic variability and the fact, that it is not one clear, chemically distinctive compound. Therefore, a lot of different quantification methods have been developed, each with different boundaries, advantages and disadvantages. **Comparisons of the methods revealed that they yielded widely varying results** (Hammes et al., 2007; Hammes and Abiven, 2013; Schmidt et al., 2001).

Following, the current state of methods in use is briefly outlined:

1. Physical methods: they usually are just a visual assessment by eye or microscope in combination with handpicking and/or counting. Often a physical separation like floatation in water is used to separate the low density PyC from heavier materials (e.g. soil minerals).

2. Oxidation methods: these methods rely on the fact, that PyC is less oxidizable than the other SOC. The CTO 375 method uses a strong acid treatment and heating to oxidize non-PyC (Bucheli et al., 2004; Gustafsson et al., 1997, 2001). The heating can be a disadvantage, as it can result in secondary PyC formation during the process (Gelinas et al., 2001). Another method uses potassium dichromate ($K_2Cr_2O_7$) to oxidize labile organic carbon, resulting in a part of PyC, which is resistant to the treatment (Bird et al., 1999; Knicker et al., 2008). UV radiation can also be used to oxidize the labile material of a sample usually followed by a characterization with NMR spectroscopy (see below) (Skjemstad et al., 1996).
3. Molecular marker methods: the benzenepolycarboxylic acid (BPCA) method relies on the fact, that under strong HNO_3 treatment, PyC breaks down into very distinctive molecules that can almost uniquely be produced in this process (Glaser et al., 1998; Schneider et al., 2011; Wiedemeier et al., 2013). These molecules can be analysed chromatographically to get a quantitative estimate of the PyC. **Furthermore, the abundance of the different BPCA marker molecules also yields information about the aromaticity and the degree of condensation of PyC** (Schneider et al., 2010; Wiedemeier et al., 2015). Since the BPCA method it is a destructive method and per definition always yields a smaller amount of PyC than the true value, **there is usually a factor of 2.27 (or ~0.4 if calibrated the other way round) used to calibrate it to the "real" content of PyC** (Glaser et al., 1998). This value has to be kept in mind for manuscripts 2 and 3, which include method comparisons between BPCA and HyPy.
4. Hydrogen Pyrolysis (HyPy): this method uses high pressure H_2 gas and high temperatures to disconnect the labile from the refractory (PyC) part of C (Ascough et al., 2009; Love et al., 1996; Meredith et al., 2012). **It is the only method, which can robustly give information on the actual detection window in the PyC continuum.** It is able to reliably quantify all aromatic compounds that have > 7 connected aromatic rings.
5. Spectroscopic methods: There are two methods, which rely on the evaluation of spectroscopic data. Solid-state ^{13}C nuclear magnetic resonance spectroscopy (NMR) can be used with a mixing model (Nelson and Baldock, 2005), but is generally combined with other detection methods. Diffuse reflectance infrared Fourier-transformed spectroscopy (DRIFT) takes advantage in the fact, that

different compounds absorb and transmit electromagnetic radiation differently (Wood, 1988). Up to now, it is only used in the combination with other quantification methods and usually rather serves as qualitative measure.

There is a set of other methods, which will not be discussed here, since they were not included in the scope of this thesis.

1.6 The Pyrogenic Carbon Cycle

Similar to the global carbon cycle, an equivalent scheme for PyC exists (Figure 4). However, the PyC cycle is not closed, but has a clear start and end, through fires and the burial in oceanic sediments, respectively. PyC is produced in natural or human-induced wildfires, which affect together nearly 4 % of the global land surface every year (Giglio et al., 2013). Due to the primary role of vegetation fires, it is assumed that most PyC is found in fire-prone systems, thus these are also the places where most research on natural PyC has focussed on to date. **During wildfires, between 15-50 % of the affected biomass is converted to PyC, while the**

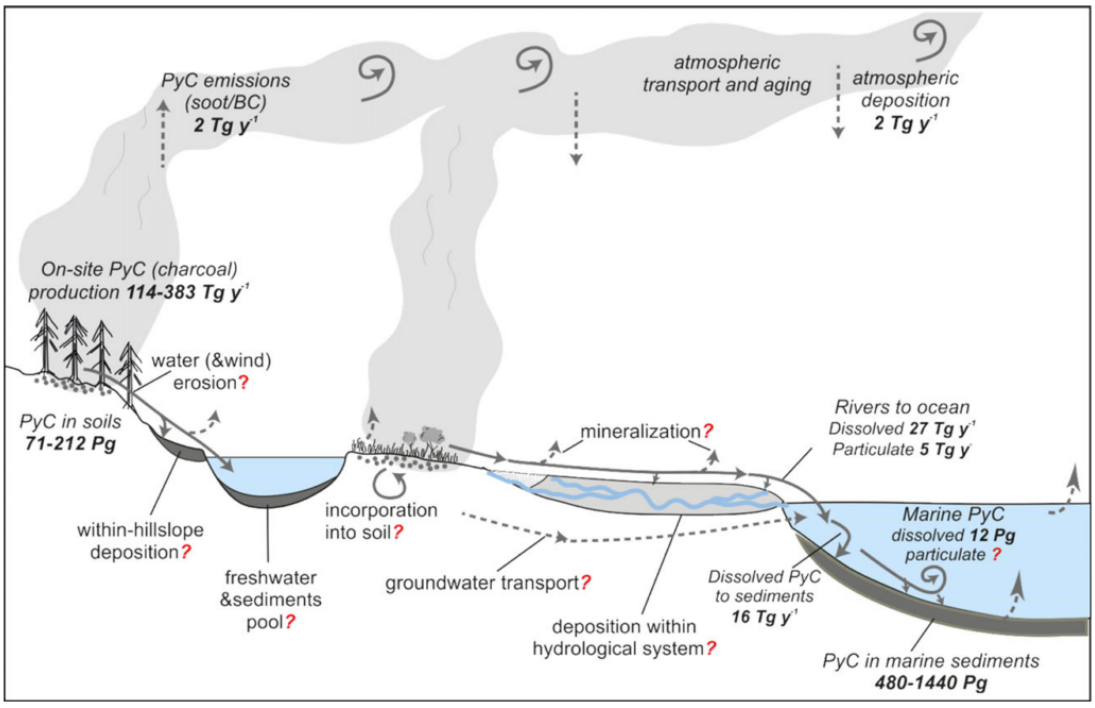


Figure 4: Global Pyrogenic Carbon Cycle. Main uncertainties and unknowns are represented by red question marks. Values are produced by different approaches and analytical methods and are only conditionally comparable; they rather serve as first estimates. (Santín et al. 2016)

rest is oxidized to CO_2 (Forbes et al., 2006; Santín et al., 2015; Tinker and Knight, 2000). As a result of fires, PyC can also be transported in the atmosphere, however, this occurs on very short time scales of only a few days or less (Bond et al., 2013). The material is then deposited on the soil surface, where it is very prone to surface erosion to lower lands or rivers in the first weeks to years (Rumpel et al., 2006; Shakesby and Doerr, 2006), which could consequently already transport the PyC to its "ultimate sites" of burial in the oceans or lakes and its respective sediments (Jaffe et al., 2013). However, if the PyC remains on the soil surface for a sufficient time, it will be incorporated into the soil matrix and become part of the SOC. In the soil, PyC undergoes very distinct and – for the global picture – highly relevant processes, which will be introduced in the next section.

The whole "cycle" is, however, only schematically described yet and important information on stocks, fluxes and processes are still unresolved. A recent review on the global PyC cycle has evaluated some numbers for the different reservoirs where PyC can be found (Bird et al., 2015), but **there is still lack of knowledge about the MRTs in different reservoirs as well as the transport mechanisms** (Santín et al., 2016). Furthermore, it is largely unknown, what the actual drivers of the different fluxes are on global as well as on smaller scales. It is questionable if numbers for landscapes or even ecosystems can be easily scaled up to the whole globe and if key drivers are the same on differing scales of observation. Thus, this thesis tries to shed some light on these unknowns.

Unfortunately, next to the "known unknowns" there are yet probably even mechanisms at work, which we are not even aware of at all, leading to contradictory or confounded results. For example, a recent study showed that subsurface flow likely transports more PyC to rivers and lakes than actual above ground runoff (Güereña et al., 2015). These findings are contrasting with other observations, which allocate a very low potential for leaching to PyC (Abiven et al., 2011; Lehmann and Joseph, 2015) while the lightweight PyC particles could be very easily moved by water above ground.

Another unresolved conundrum is the mismatch between the age of PyC found in watersheds and the ocean (> 1500 years), compared to the actual MRTs of PyC in soils (100 - 1000 years). Thus, PyC has to "pre-age" somewhere or to be retained strongly in certain environments, before it reaches the sea (Cotrufo et al., 2016; Hanke et al., 2017; Raymond and Bauer, 2001).

But it is not only interesting and important to look at the burial of PyC in sediments, which represents the removal of the material from the carbon cycle over geological timescales, it is in the same way crucial to understand how the PyC mineralizes back to CO_2 and stays in the actual carbon cycle. **Both pathways can be very prominent in soils, thus understanding the dynamic role of PyC in soils helps us to understand its fluxes towards both the atmosphere as well as to long-term stabilization**.

1.7 Pyrogenic Carbon in Soils

PyC can be found in all ecosystems and is literally ubiquitous in soils around the world (Preston and Schmidt, 2006). However, quantities and the spatial distribution of PyC in soils are poorly resolved. The heterogeneity is apparent from current literature with widely varying values, but cannot be explained, yet. Many different estimates of the content of PyC in total SOC exist on global scale (Forbes et al., 2006; Hockaday et al., 2007; Preston and Schmidt, 2006), as well as for a set of different ecosystems, mainly being boreal forests (Bay, 2014; Guggenberger et al., 2008; Ohlson et al., 2009), temperate grasslands (Glaser and Amelung, 2003; Schmidt et al., 1999; Vasilyeva et al., 2011) or subtropical savannahs (Andreae et al., 1996; Beringer et al., 2007; Lehmann et al., 2008). **The spread of values in these studies is covering nearly the whole spectrum from < 1 % to more than 60 % of SOC**. Estimations of global PyC stocks based on such values range from 54 – 109 Pg C (Bird et al., 2015) to 72 – 212 Pg C (Santín et al., 2016).

The picture looks very similar regarding the actual MRTs of PyC in soils. Estimates have significantly changed over the last decades from < 100'000 years (Goldberg, 1985) over 10'000 years (Schmidt et al., 2000) and 2000 years (Kuzyakov et al., 2009) to more recent estimates of centennial timescales (Lehmann and Joseph, 2015; Maestrini et al., 2014a; Singh et al., 2012; Zimmermann et al., 2012). Again, the value of MRT can vary significantly based on the environmental properties and the feedstock material. Decomposition, stabilization and destabilization are highly variable processes, which are difficult to grasp, even more so on large spatial scales.

But PyC does not only have a direct influence on the carbon cycle through the high MRTs, **it can also affect the residual SOC, by stimulating or inhibiting microbial decomposition. This phenomenon is called priming effect** (PE; Bingeman, Varner, and Martin 1953). If the decomposition of SOC is promoted by input material (such as natural PyC or biochar), we speak of positive priming,

whereas we speak of negative priming, when decomposition is inhibited. Research on PyC input has shown that the PE can be positive (Luo et al., 2011; Wardle et al., 2008), negative (Cross and Sohi, 2011; Kuzyakov et al., 2009) or have no direction whatsoever (Abiven and Andreoli, 2010; Santos et al., 2012). However, in a meta-analysis it was shown that overall, PE is positive in the first months after addition and becomes negative after around a year (Maestrini et al., 2014b), but results are only vague and do not extend more than 2 to 3 years.

The PE is highly relevant, since it could turn the potential of PyC to persist in the soil for long times into a disadvantage, if the decomposition of SOC gets stimulated by it over very long timescales, such that more carbon is decomposed as PyC had initially entered the soil. Until now, only limited quantitative and mechanistic knowledge off PEs exists and was mainly derived from short term and/or lab-incubation studies. Moreover, we have very little information about its importance in different ecosystems.

2 Objectives and Research Questions

„I have steadily endeavoured to keep my mind free so as to give up any hypothesis, however much beloved (and I cannot resist forming one on every subject), as soon as facts are shown to be opposed to it.“

Charles Darwin

As seen in the introduction above, PyC is highly relevant in the global carbon cycle, but poses several challenges to detailed investigations. Its spatial distribution is only marginally explained on global as well as on landscape or even plot levels. No uniform method to robustly quantify and characterize PyC exists. Moreover, the spatial component of decomposition and stabilization patterns is poorly understood, too. Therefore I surveyed, estimated, examined and analysed PyC on a set of different scales and with different approaches. Here I provide a conceptual framework, to guide the reader through the different spatial scales and objectives of this thesis (Figure 5).

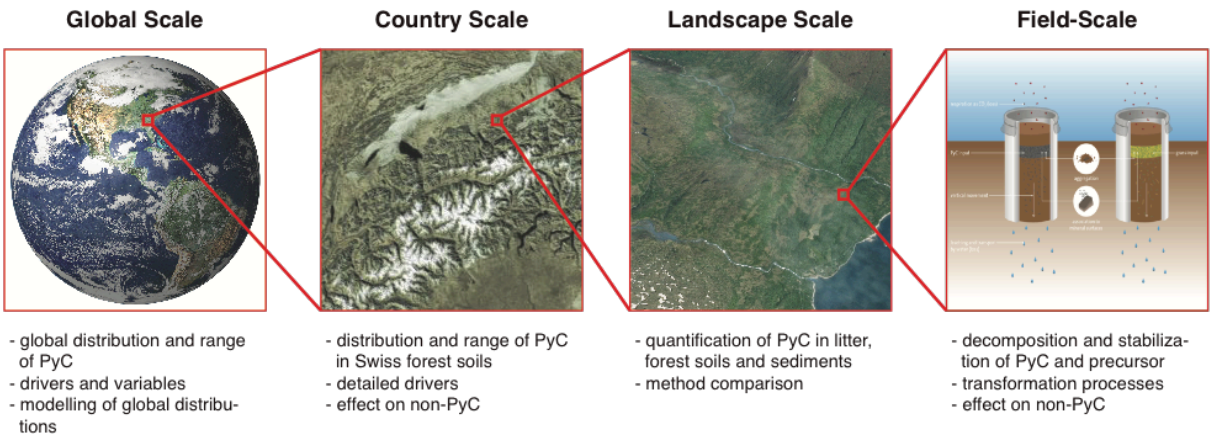


Figure 5: Scheme of the different chapters and their covered topics from this thesis. Pictures have symbolic character and do not necessarily represent the exact location where the study was done.

2.1 Global Scale – Distribution Patterns

The aim of the first study was to get an as comprehensive as possible overview upon the global distribution of PyC (chapter 1). Main research questions and objectives were:

1. **What are the PyC contents and stocks in different ecosystems?**
   How are contents different under different fire activity, climate region or land use?

2. **Which are the drivers explaining the distribution of PyC best?**
   Out of a large set of possible drivers like soil properties, climate, land use or vegetation cover.

3. **Model the global distribution of PyC using significant drivers found in research question 2.**

2.2 Country Scale – Drivers of PyC Content and the Effect of PyC on SOC dynamics

This part of the thesis examined the relationship between ecosystem properties with PyC quantities and quality on the example of Switzerland (chapter 2). A large database enabled us to select samples based on climatic, landform and soil property drivers. We used the BPCA and the HyPy method to relate these drivers to PyC. We could furthermore use ^{14}C and laboratory decomposition data of the respective SOC to investigate the relation between PyC and the short- and long-term decomposition patterns of SOC. Research questions were:

1. **Which drivers explain the content/stocks of PyC in Swiss forests?**
   Do we find the same drivers as in the first, global study?

2. **How does PyC content relate to the turnover of SOC?**
   Is there a positive or negative priming effect?

3. **What is the relation between the results of the BPCA and the HyPy method?**
   Comparison between the two methods regarding quantification.

2.3 Landscape Scale – Method Comparison of PyC across a Landscape

In this study (maunscript 3), we strived to improve our possibilities to reliably quantify PyC not only in soils, but also other environmental matrixes. We used three different methods to quantify PyC in free form, fresh plant litter, soil and sediment. The BPCA, HyPy and DRIFT method were compared to each other to see if it was possible to correct certain methods against each other. Research questions were:

1. **What is the relation between the results of the BPCA and the HyPy method?**
   Comparison of the quantities measured with both methods. Find a linear relationship.

2. **How is that relation different in different matrixes?**
   Is there a difference in the relationship in sediments, litter or soil?

3. **Can DRIFT be used as a cheap and fast method to substitute for these methods?**

2.4 Field Scale – Decomposition vs. Stabilization of PyC

Next to our investigations on contents and stocks around the world, in Switzerland and the attempt to improve our quantitative methods, we also examined the actual decomposition and transformation patterns of PyC happening in nature. To achieve this, we conducted a field experiment on three very different sites with small mesocosms and artificially produced grass-PyC (chapter 4). On the three different sites we furthermore investigated potentially critical drivers of decomposition, which should be specific to the respective site. Lastly, we could also calculate the impact of PyC input on the native SOC through the PE. This study closes the circle of our different scales, by not only looking at the processes and variability of PyC on the

scale of meters and less but using three different sites from tropics to the arctic, moving it back into a global perspective. Research questions in this study were:

1. **How fast do grass and grass-PyC inputs decompose in the different ecosystems?**
   Comparison of recoveries among ecosystems and inputs.

2. **How are the two materials stabilized in aggregates and on mineral surfaces?**
   Using a density fractionation method to distinguish between the untransformed, aggregated and bound on mineral forms.

3. **What influence do the site-specific drivers have on decomposition and stabilisation?**
   How important are specific drivers like pH or soil moisture for the recoveries?

4. **What direction and magnitude has the PE under all these treatments?**
   How important is the PE quantitatively and is it predictable?

3 Material, Methods and Study Sites

"Something my father dearly loved was the scientific method, and it's founded in this element of humility. The idea is that you pursue the truth wherever it goes; you need to evidence, and you can – you see if it's repeatable."

Nick Sagan

3.1 Global Distribution of PyC

To answer the research questions highlighted in the objectives part on the global scale we created a literature inventory. The goal was to retrieve as much data as possible on both PyC contents and its respective drivers from the available literature, creating a large database of published PyC values and metadata. We then used a modelling approach to estimate global distributions of PyC contents and stocks.

Data Retrieval

All data was collected with a literature screening by using keywords corresponding to PyC in soils. Only data from "natural" PyC was included, while artificial inputs of PyC from biochar or as archeological residues were discarded. Additionally, information corresponding to fire history or regime, climate and soil properties was collected from the respective articles. If not already given in the articles, climatic data was extrapolated from open access meteorological data and land use was fitted from the MODIS land cover data (Friedl et al., 2010). Furthermore, fire regimes (pyromes) were fitted from a global dataset of Archibald et al. (2013).

Modelling

We used the site information form the publications and the additional extrapolated climate and land use data to fit a linear model to explain the PyC contents in the total SOC. Only statistically significant parameters (p-value < 0.05) were included in the model. The resulting model is shown in equation (1),

$$\log(\text{PyC}) = \text{clay} + \text{pH} + \text{MAP} + \text{MAT} + \text{land use} + \varepsilon \quad (1)$$

where PyC is the PyC content as % of SOC, clay is the clay content in %, MAP is the mean annual precipitation, MAT is the mean annual temperature, land use is the different categories of land use from the database and ε is the residual error, or the

remaining unexplained variance. For more details on the parameters, see manuscript 1.

With this model we predicted the PyC content on a global scale using global datasets for the respective model variables. Soil properties were taken from the harmonized world soil database (HWSD; FAO/IIASA/ISRIC/ISSCAS/JRC (2012)), climatic datasets were taken from New et al. (2002). By multiplying the PyC contents with SOC stocks (also from HWSD), we could furthermore model the PyC stocks.

3.2 Drivers of PyC Content and the Effect of PyC on SOC dynamics on the Country scale

Here we could use a statistically refined dataset to test drivers independently, developing the research question on the drivers of PyC also for a smaller scale than the whole globe. We used two methods of quantification to find relations of both quantity and quality of PyC with its proposed drivers as well as the turnover of SOC. Two turnover times of SOC, one for relatively short-term turnover and one for rather long-term turnover could be used to correlate with PyC contents and answer research question two. We could then also compare the measured PyC contents of both methods against each other.

Site selection

We used data from a large database of Swiss soils from the Federal Institute of Snow, Landscape and Forestry (WSL). Fifty-four sites were selected in the process of an earlier study (González-Domínguez et al. in rev.). The selection was based on large range of climatic conditions, soil properties (in particular clay content and pH) and landforms, such that all the variables were nearly independent, allowing for robust statistical evaluation. A detailed description of the site selection, the sampling and the WSL database is given by González-Domínguez et al. (in rev.) or manuscript 2 and its supplementary material.

BPCA

We used the BPCA method to quantify and characterize the PyC. The method has been going through some development in the last years (Glaser et al., 1998; Schneider et al., 2011; Wiedemeier et al., 2013) and the most recent description is given in Wiedemeier et al. (2016). As already discussed briefly in the introduction, this method does not quantify the material itself, but the chemical products of PyC after strong HNO_3 treatment for 8 h on 170 °C. The resulting extract is purified using

cation exchange resin and solid phase extraction. Afterwards, the derivatised compounds are analysed on a liquid chromatograph. BPCAs having 3, 4, 5 or 6 carboxyl groups are quantified there and can be summed up for the total PyC_{BPCA}. The relative amount of B6CA gives an indication on the degree of condensation of the initial PyC (Schneider et al., 2010; Wiedemeier et al., 2015).
This method was also used for chapter 3, the method comparison across a landscape.

HyPy

This method is known to quantify precisely the amount of PyC containing < 7 fused aromatic rings, implying that it also quantifies geological graphitic structures (which is not the case for BPCA). Recently, it has been started to be used for quantification of natural PyC or archaeological residues (Ascough et al., 2009; Meredith et al., 2012). The soil samples are loaded with a molybdenum catalyst using an aqueous/methanol (1:1) solution of ammonium dioxydithio-molybdate ($(NH_4)_2MoO_2S_2$). The loading represents around 1 % of the sample weight. The samples are then laced in the HyPy reactor, where they are pressurized using hydrogen gas at 15 MPa with a sweep gas flow of 5 L min^{-1}. Samples are first heated with a rate of 300 °C min^{-1} to 250 °C and afterwards further heated at a rate of 8 °C min^{-1} to a final temperature of 550 °C, which is held for 2 min. After cooling down, the samples can be retrieved from the reactor and the residues measured for C with an elemental analyser.
This method was also used in chapter 3.

Turnover times

Turnover times (or MRTs) for bulk SOC were calculated in the study from González-Domínguez et al. (submitted). The short-term turnover times (τ_{short}) were based on an incubation experiment of around six months and calculated from the respired CO_2. The range of τ_{short} was 5 - 29 years for all the samples. Based on the radiocarbon signature of the bulk SOC another turnover time (τ_{long}) was modelled, representing the longer timescales with a range of 67 - 511 years for all the samples. The detailed procedure of both turnover times is given in González-Dominguez et al. (in rev.) or the supplementary material thereof.

3.3 Method comparison of PyC across a landscape

We used the same two methods BPCA and HyPy, which are already described above, to compare for PyC contents in a set of environmental matrixes in a

watershed. Furthermore, DRIFT was used on the samples to predict BPCA and HyPy methods with the help of partial least square regression (PLSR).

Study Site and sampling

The study was conducted in a watershed northwest of Fort Collins, CO, USA. This specific area had suffered wildfires in 2012 (Boot et al., 2015). Samples were taken from mineral soils and organic litter of the pine forest floor as described in Boot et al. (2015). Sediment samples were taken directly at the river Cache La Poudre. Pure PyC was provided from private companies (Biochar Solutions Inc., USA and Biochar Now, Inc., USA). A detailed sampling scheme is given in manuscript 3. The three methods comprise BPCA, HyPy and DRIFT, of which the first two were already briefly discussed above.

DRIFT

DRIFT spectroscopy uses a range of wavelengths to characterize all kind of materials. The wavenumbers lie in the infrared region and span from 4'000 to 400 cm^{-1} (equal to wavelengths of 2.5 to 25 μm). The samples are milled, oven-dried and homogenized. Spectra are then recorded using potassium bromide (KBr) as reference, which does hardly absorb in the infrared region at all. Absorption bands for typical PyC functions (aromatic groups) are given from earlier literature (Baldock and Smernik, 2002; Guo and Bustin, 1998). To calibrate this method, a PLSR was used. This statistical method results in several factors with decreasing explanatory power. As few factors as possible are then taken, which still explain the most of the variance in the dataset.

It is important to state here, that DRIFT does not work without a reference or training dataset. In this case, the BPCA and HyPy data could be used for training and validation. Otherwise, one would require other information on the PyC content for the calibration part.

3.4 Decomposition vs. Stabilization of PyC

To answer the research questions of chapter 4 we used highly ^{13}C labelled ryegrass and PyC produced from it and buried it in the soil of three very different ecosystems. By introducing site-specific drivers as additional treatments we could check whether differences in pH or moisture level were also inducing an effect similar to the big differences between the three ecosystems. We applied a density fractionation method to investigate different processes of stabilization. To calculate the priming

effect we used the difference between SOC content of the treatment and the control at the end of the experiment.

Study sites

Three study sites were used to compare the decomposition and transformation pathways of grass and grass-PyC. The three sites represent three extremely different ecosystems: a tropical evergreen forest, a temperate mixed forest and arctic tundra. The first site lies in the pristine tropical forest of Lambir Hills National Park (4°12' N, 114°02' E) on the island of Borneo and features warm and wet climate with around 27 °C mean annual temperature (MAT) and 2740 mm mean annual precipitation (MAP). Soil was classified as an Arenosol. The second site lies on the Lägeren mountain range in Switzerland (47°29' N, 8°22' E). MAT is 8.4 °C and MAP is 930 mm. Here, part of the samples was taken on a Leptosol and part on a Cambisol (as part of the site-specific treatment). The third site lies in the Kytalyk Nature Reserve in the arctic tundra of northeast Siberia, Russia (70°49' N, 147°28' E). The climate is extremely continental with a MAT of -13.1 °C (and a range of more than 60 °C over the course of a year) and a MAP of 232 mm. Tundra sedges, mosses and dwarf shrubs dominate the landscape. Soils are classified as Histic Cryosols.

More information on the sites is given in chapter 4 or the supplementary material thereof.

Design

On each site, we placed small steel cylinders (mesocosms) in the topsoil (diameter ~7 cm, height ~12 cm), in which highly ^{13}C labelled grass or PyC were buried 1 cm below the soil surface. A third of the cylinders served as control and received no treatment. On each site, an additional site-specific treatment was used, to investigate whether site-specific differences in important drivers might be more or less relevant than differences between ecosystems. In the tropical rainforest, half of the samples received reduced rainfall (~ 20 %), in the temperate forest, half of the samples was situated on acidic soil, while the other half was on calcaric soil, but less than 50 m apart. In the arctic tundra, half of the samples had the groundwater penetrate the cylinders, while the other half was placed on drier ridges. A similar sampling scheme was also used by Singh et al. (2014) and Maestrini et al. (2014). An overview is given in Figure 6, where also the processes are shown, which were investigated using the density fractionation method and the ^{13}C recovery.

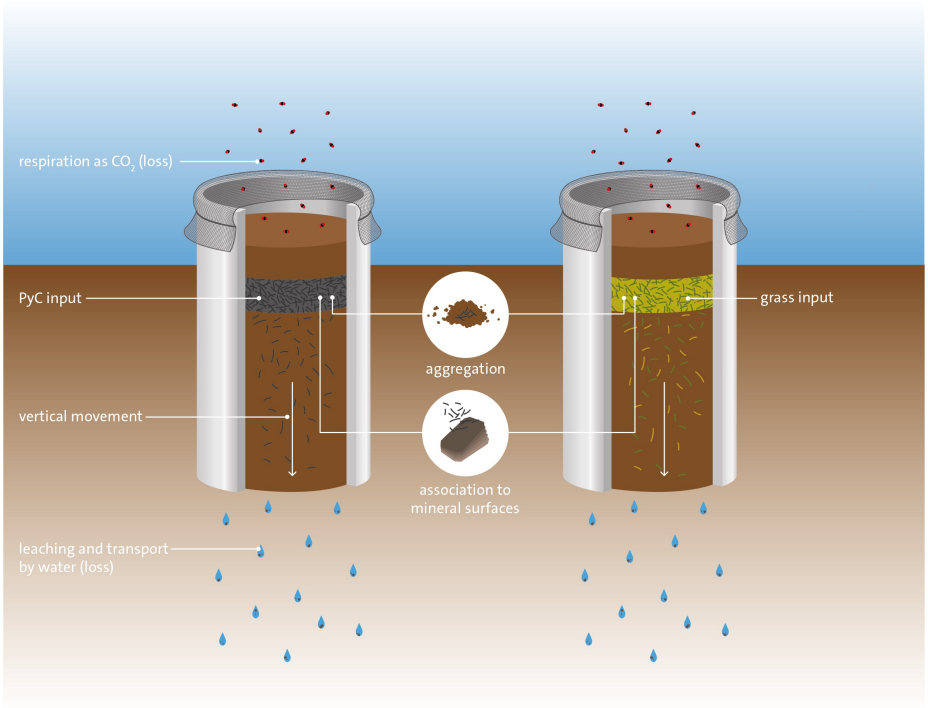


Figure 6: Conceptual Design of the field-experiments. Shown are two exemplary mesocosms, which can contain either PyC or grass as input material (or no input for control). Investigated transformation processes are depicted for both materials. Aggregation and association to minerals were studied using the density fractionation method, vertical movement was studied by slicing the soil in three different horizons in the sampling process. Respiration and loss through leaching and water transport represent together the difference between input and recovery of the material. (Manuscript 4)

Density Fractionation

The density fractionation method used here allows us to divide the SOC in different pools of varying transformation phases. The first pool is the untransformed input material (free light fraction; fLF) defined as the material that floats freely on a 1.6 g cm^{-3} density solution (sodium polytungstate; SPT) after centrifugation. The second pool can be divided by using ultrasonic dispersion with a disruptive energy of 250 J ml^{-1}. The material, which is floating on the SPT solution after ultrasonic dispersion and reapplied centrifugation is supposed to represent the SOC bound in aggregates and is defined as occluded light fraction (oLF). The remaining material is defined as heavy fraction (HF) and the SOC therein is considered to be strongly associated to minerals.

^{13}C recovery and mixing model

To measure the recovery of the input material, we took subsamples of three different depths (0-3 cm, 3-6 cm and 6-10 cm) and all the density fractions (which were all

done on the 0–3 cm depth). They were then measured for bulk C content and ^{13}C signal with a Picarro device (Picarro Inc. USA). The recovery of the initial input can be calculated based on the Picarro measurements using equation (2),

$$m_{recover} = \frac{f_{sample} * m_{sample} - f_{control} * m_{sample}}{f_{material} - f_{control}} \quad (2)$$

where $m_{recover}$ is the mass of labelled input C that is still there, f_{sample} is the ^{13}C atom fraction in the taken sample, m_{sample} is the mass of the sample, $f_{control}$ is the ^{13}C atom fraction of the closest control sample, and $f_{material}$ is the ^{13}C atom fraction of the input material.

Priming

Usually, priming is calculated as the relative increase in C mineralization of a treated sample compared to a control sample. Disadvantage is that measurements are very discrete in time and if a time series is targeted, one needs to monitor the mineralization regularly for all the samples. We here used the stocks of treatment samples and control samples to get an integrated PE over the whole period of time of the experiment. Thus, our values are not directly representing change in mineralization, but rather the consequence thereof after the duration of the experiment and are hence also not directly comparable to most published values on the PE.

Briefly, the PE was calculated by comparing the SOC mass of a mesocosm, which had received input (corrected for the respective input) to the closest control mesocosm (usually < 15 cm apart). The relative difference could be calculated using equation (3),

$$PE\ [\%] = \frac{C_{treatment} - C_{control}}{C_{control}} * 100 \quad (3)$$

where $C_{control}$ is the carbon content of the closest control sample, $C_{treatment}$ is the carbon content of the sample, corrected for the respective carbon input.

4 Results and Discussion

„What matters is not the facts but how you discover and think about them.“

Richard Dawkins

4.1 The Global Distribution of PyC

Our results highlight that PyC is not only quantitatively important on a global scale, but also that fire plays (at least measured with remote sensing) a minor role, compared to soil properties, when it comes to the explanation of contents. All results are given in content of SOC, since the majority of articles reported it in this way and lacking BDD values hampered calculation to stocks.

PyC contents

Figure 7 presents the PyC contents in the SOC in the complete dataset. Half of the values lie between 5.2 and 18.6 %, while the arithmetic mean is located at 13.7 %.

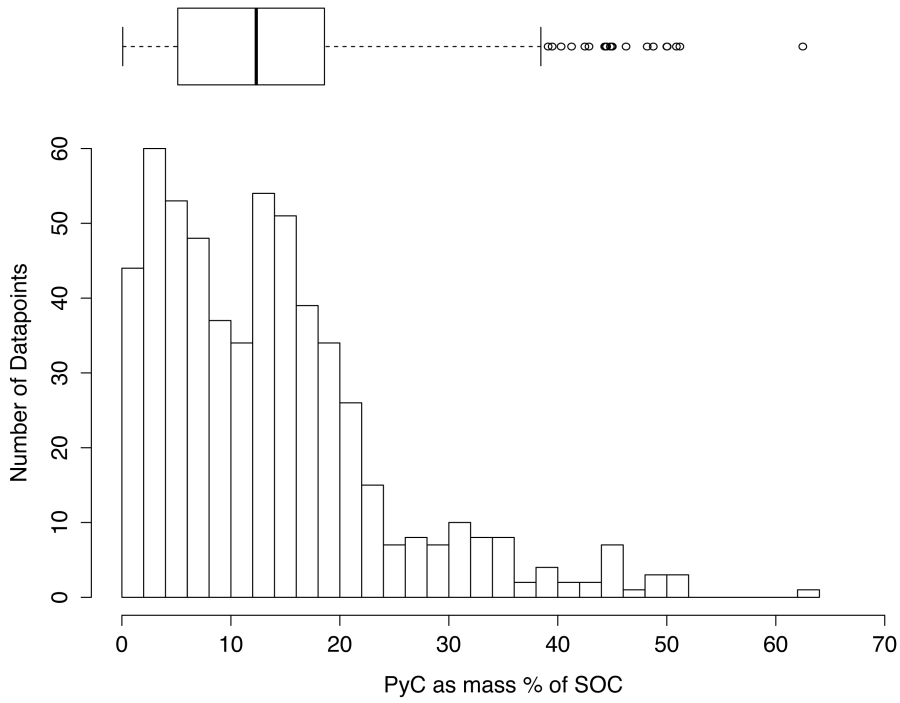


Figure 7: Frequency histogram of PyC content as mass % of SOC for the entire database (n=569). Each column represents an increment of 2 %. (Manuscript 1)

The range we found was from 0.1 to 60 %, and therefore broader than previous estimates (Bird et al., 2015; Forbes et al., 2006; Santín et al., 2016). If this 13.7 % is compared to other identifiable compounds, it is apparent, that it represents a very large amount. Carbohydrates can be found in similar extends of 5 to 20 % (Lowe, 1978), lignin ranges from 0 to 6 % (Thevenot et al., 2010) and soil lipids never even make up more than 2 % in general (Dinel et al., 1990). **Our results emphasise that PyC is not only important through its unique chemical and physical properties, but also because it is quantitatively a major compound class in soils on the global scale.**

There is a set of limitations to these results. The values represent a mix of all different kinds of methods (briefly discussed in the introduction), mirroring in fact very different sections of the PyC continuum or operationally defined compounds (Hammes et al., 2007). Astonishingly, over this large dataset all methods nonetheless yielded results in the same range. Therefore, we could combine all the methods without calibration to a single “key-method”. These results imply that the values from different methods average out, when used about a broad range of soils. However, the data was also not geographically balanced, since the majority of values were retrieved from Central and Eastern Europe or North America, while very few data exist for Africa, South America or most parts of Asia.

Drivers of PyC

Some very surprising results were found for the correlation of environmental variables. **Fire data like the fire return interval, fire activity proxies (Chuvieco et al., 2008) or pyromes (Archibald et al., 2013) could hardly explain any variance in the dataset.** We could only find a correlation, if site-specific fire information was given. This indicates, that fire does not play a crucial role in driving PyC contents on large scales, but only locally. Furthermore, transport by air is probably small, since we should otherwise see a better fit with the global fire datasets (integrating over bigger areas).

Strongest drivers of PyC contents seem to be much more related to stabilization processes than actual input, as clay content and pH were explaining most of the variance in the data (**Error! Reference source not ound.**), followed by temperature and precipitation. Clay content might possibly drive organo-mineral interactions with its high and reactive surface area (Hassink, 1997; Merckx et al., 1985; Six et al., 2002). The story with pH is a bit more complicated. On one hand, a high pH is usually related to high decomposition (Aciego Pietri and

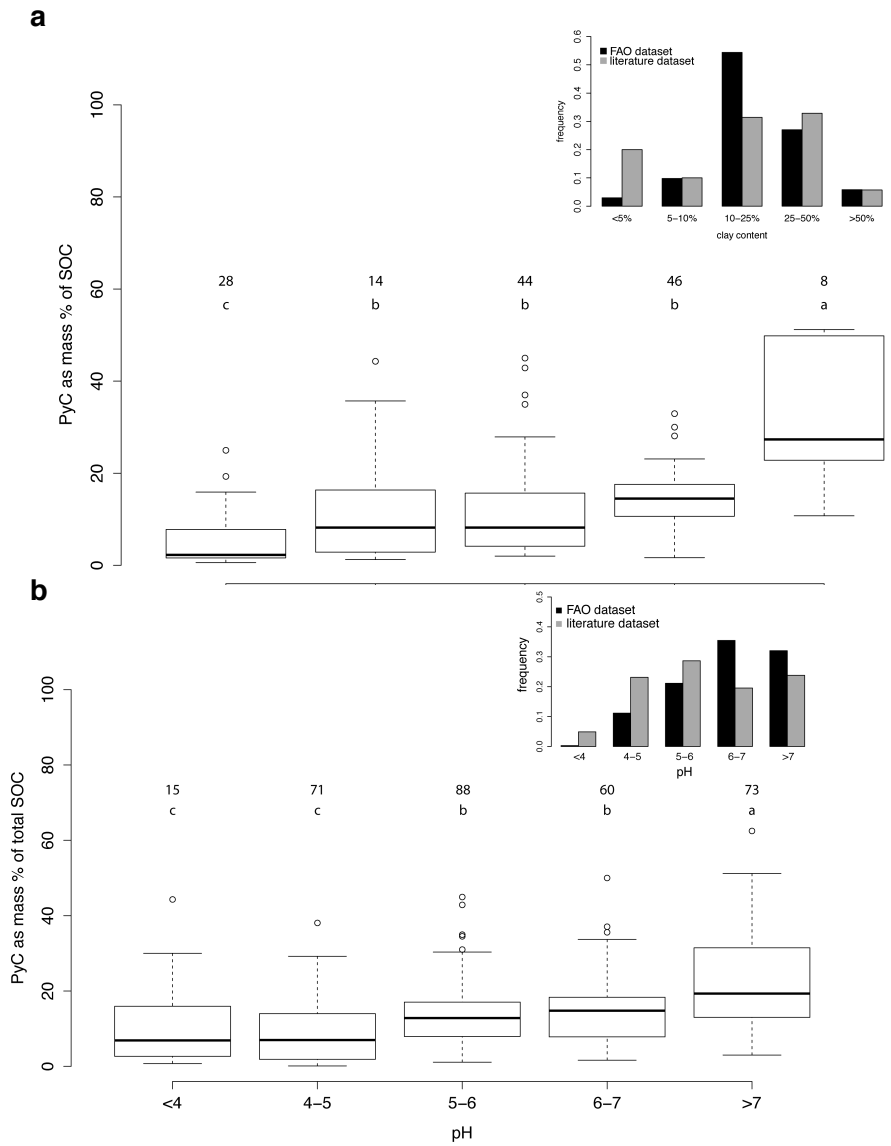


Figure 8: PyC as mass % of SOC described by a) clay content and b) pH value. Letters indicate significant differences between groups ($p < 0.05$) within the respective dataset. On the top-right corner, the distribution is shown as compared to the global FAO dataset. If grey and black bars are very differently distributed, it means that the data is not well balanced / representative on the global scale. (Manuscript 1)

Brookes, 2008; Kemmitt et al., 2006) and it is well known among archaeologists to look for PyC in low-pH soils (Braadbaart et al., 2009), on the other hand, PyC fragmentation seems to be increased under alkaline conditions (Braadbaart et al., 2009). This might then lead to either a better incorporation into the soil profile, stabilization through increased surface area (Nocentini et al., 2010), but potentially also a better volatilization and consequently evacuation by water.

Land use also relates to PyC contents. Agricultural soils for example show the highest contents among all the land uses. However, it is not clear, if PyC is increased due to higher inputs through stubble-burning or slash-and-burn practices (Peters and Neuenschwander, 1988; Wiedner and Glaser, 2015), or if farmers tended to look for nutrient rich soils, which often coincide with high PyC contents.

We could see that it is crucial to consider both spatial and temporal scales, when relating PyC to environmental variables. The weak correlation of fire can be explained by a mismatch of both temporal as well as spatial scales, since global estimates only exist for the last two decades and global resolution is still very coarse, while PyC varies only with the exact locations of fires and its MRT is at least one order of magnitude higher than all global fire data. Soil properties on the other hand change very slowly and thus can be taken as constant over the turnover times of PyC, playing an equally important role over this whole period.

A global prediction of contents and stocks

Using the five variables explaining the most variance of our dataset (clay content, pH, temperature, precipitation and land use) as input for the model, we could predict a global distribution. Figure 9 shows the results from this linear prediction model. Using global datasets on SOC content in soils as well as bulk dry density we could further calculate estimates of global PyC stocks. Figure 9 shows, that the distributions of contents and stocks look rather different, meaning high PyC contents are often found in regions with low SOC content and vice versa. Therefore, highest stocks can be found in the extremely SOC rich boreal and arctic regions, as well as the tropics. With integration of the data from this prediction we get a rough estimate of 200 Pg of PyC for the world soils up to 2 m depth, which lies on the upper limit of previous estimates (Bird et al., 2015; Santín et al., 2016).

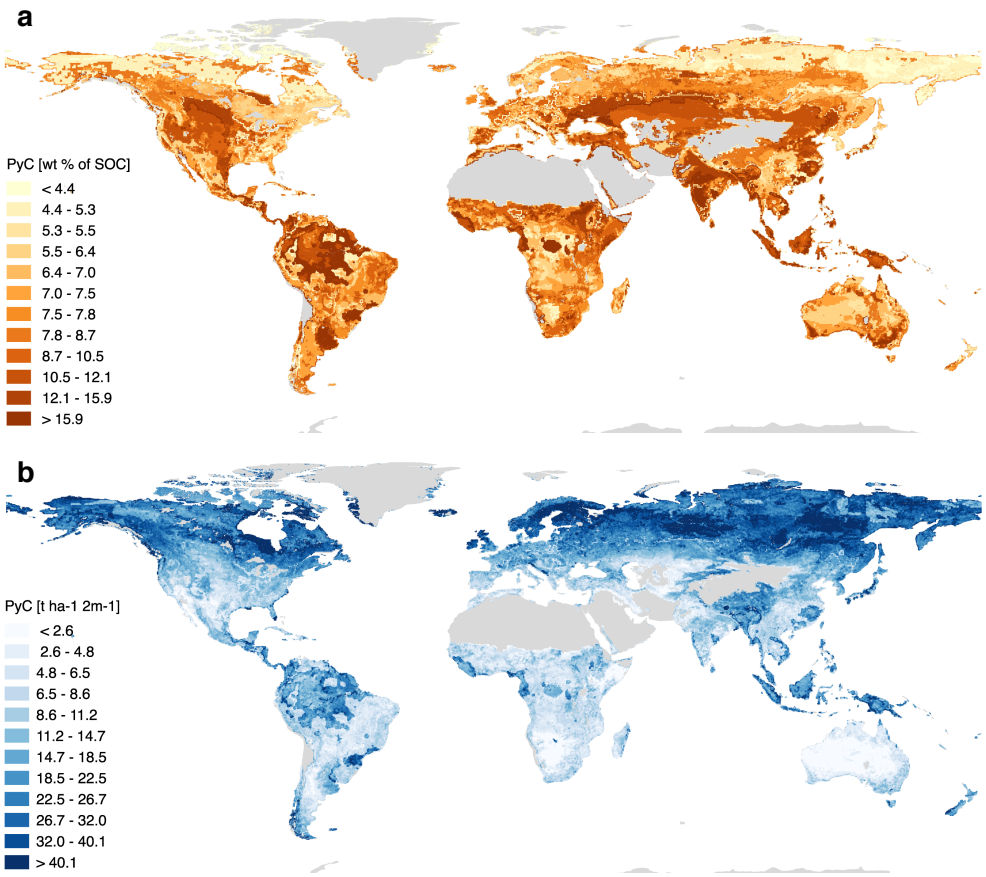


Figure 9: Predicted global PyC contents in mass % of SOC (a) and stocks in tons per hectare of the first 2 m of soil (b). Explained variance of the linear model is 33 %. Landmass is coloured in grey. (Manuscript 1)

4.2 Drivers of PyC Content and the Effect of PyC on SOC dynamics on the Country Scale

After the interesting results in the above-mentioned global study, we could further investigate the relations of the same drivers on a smaller, better constrained dataset in Switzerland. Here, soil properties, landform and climate are nearly independent and provide a wide range of values. Climatic conditions e.g. range from Mediterranean to boreal climates. Further variables like land-use (all forest soils) and fire characteristics are kept more or less constant over the range of data in this study.

Drivers of PyC content

Similarly to the global study, the results show that soil properties are the strongest explanatory variables of PyC contents in the SOC. Clay content is significantly positively related to the PyC content measured with the BPCA method (PyC_{BPCA}), whereas pH and precipitation are significantly related with the PyC content measured with the HyPy method (PyC_{HyPy}). A higher pH value and drier climate generally favour high PyC contents. **Therefore, we can on one hand support our previous findings that soil properties are the main drivers of PyC content. However, on the other hand it is also apparent that there are differences in the climatic drivers and between the results of the two methods.** While on the global scale only temperature is a significant driver of PyC (as seen in 4.1), this was not found on the scale of Switzerland. Here, only precipitation is significant.

We could not find any evidence for a relation between landform (slope, orientation) and the PyC content. Slope is usually a very important indicator of erosion and PyC can be eroded preferentially compared to bulk SOC (Cotrufo et al., 2016; Rumpel et al., 2006). However, the relevance of erosion is likely the highest shortly after a fire, when the PyC is still lying on top of the soil surface. Our dataset does not feature recent fires (with one outlier), thus (preferential) erosion does probably not play a role anymore here, explaining why there is no apparent correlation.

Relation of PyC with SOC turnover

We found interesting relationships between τ_{short} and τ_{long} of SOC and the PyC_{BPCA}. Namely, the B5, one of the BPCA compounds, which stems from relatively condensed structures, is positively correlated to τ_{short}. **This indicates, that PyC has an impact on the dynamics of SOC, even if its input dates back decades to centuries**. The aromatic structures of PyC, providing pore-space and

large surface areas, could potentially stabilize SOC and slowing down turnover of otherwise labile compounds. The B5 fraction of the BPCAs might just explain this stabilizing part of PyC. However, mechanisms behind the relation between B5CA and τ_{short} are very speculative and would require another set of experiments to observe and verify our speculations about them. Yet, if we assume that the PyC in the samples is decades to centuries old, **our results suggest influence of PyC on SOC turnover of timescales which are one to two orders of magnitude higher than anything observed before** (Maestrini et al., 2014b). Even though what we see cannot be accounted as PE sensu stricto (because we do not have control samples with zero PyC and do not know the real ages of the PyC), it still gives a strong indication of it.

We found another relation between τ_{long}, modelled from bulk SOC ^{14}C data, and the B6CA fraction from the BPCA method. Here, it is more likely the high age and low turnover leading to an increased relative proportion of B6, rather than the B6 influencing the turnover. Intuitively, ageing of PyC leads to a preferential preservation of its most stable components, as the more labile ones are decomposed first. These stable components are most likely the large and structured aromatic sheets, with little reactive groups as "attacking points" for decomposition. Alternatively, it could also be possible, that B6 is influencing even τ_{long} directly (in the same way as B5 and τ_{short}).

PyC_{HyPy} did not correlate with any of the turnover times. Since PyC_{HyPy} is believed to be purely quantitative, it seems like the chemical structure of the PyC (captured with the BPCA method) is very important, when it comes to stabilization of SOC (or priming).

Comparison of the two methods

Additionally to the relations of ecosystem properties with PyC contents, we could compare the two methods with each other. It was possible to establish a linear relationship between PyC_{HyPy} and PyC_{BPCA}. A linear regression model resulted in the following equation (1):

$$PyC_{BPCA} = 1.02 + 0.21 * PyC_{HyPy} \quad (1)$$

Both intercept and slope were statistically strongly significant ($p < 0.001$). R^2 is only 0.5, thus the explained variance leaves large gaps, however, it gives a good first impression on the relation between PyC_{HyPy} and PyC_{BPCA}. Prominent is the high intercept of 1.12, indicating a relatively large and constant proportion of PyC, which

cannot be detected by the BPCA method. Such a proportion is most likely originating from the very upper limit of the PyC continuum, characterized by very condensed and aromatic molecules. However, it remains difficult to disentangle the different possible origins of the PyC in the continuum. This method comparison is further limited by the use of forest soils alone. A more differentiated method comparison, using also different environmental matrixes is described in the next chapter.

4.3 Method comparison on PyC across a landscape

Here, it was possible to correlate measured BPCA and HyPy values for all kind of samples of one watershed. However, the linear regressions vary between different environmental matrixes, meaning that e.g. soil and litter have to be corrected differently. An overview of the linear relationships between PyC_{BPCA} and PyC_{HyPy} is given in Table 1. Always explaining more than 74 % of the variance, these linear relationships are generally describing more of the variance in the data than on the bigger scale of Switzerland and represent powerful tools to calibrate the different

Table 1: Linear relationships between PyC_{BPCA} and PyC_{HyPy}. *Reported *p*-values refer to the significance of fit. *p*-values for intercepts were never significantly different from 0. (Manuscript 3)

Matrices	*n*	Linear fit	R^2	Adj R^2	*p* value*	Pair-wise
Char	5	$PyC_{BPCA} = 3.66 + 0.10 * PyC_{hypy}$	0.92	0.90	0.0094	a
Fire layer	6	$PyC_{BPCA} = 2.06 + 0.17 * PyC_{hypy}$	0.74	0.68	0.0272	ab
Forest floor	14	$PyC_{BPCA} = 0.18 + 0.25 * PyC_{hypy}$	0.76	0.74	<0.001	b
Soil	41	$PyC_{BPCA} = 0.05 + 0.23 * PyC_{hypy}$	0.89	0.89	<0.001	b
Sediment bank	16	$PyC_{BPCA} = -0.99 + 0.44 * PyC_{hypy}$	0.82	0.81	<0.001	c

methods to each other. It is also noteworthy, that the intercept in forest soils is much lower than in the Swiss study and not significantly different from zero. This indicates that there is a fraction of PyC, which could only be detected by the HyPy method in the Swiss forest soils, but not in this landscape. However, it was shown in previous method comparisons, that the same methods could yield varying results if conducted in different labs (Hammes et al., 2007; Hammes and Abiven, 2013), which was the case for these two chapters. Therefore, it would be interesting to look a bit further into the comparison between the forest soils from both studies and test, whether different results are rather originating from slightly varying procedures or from the varying ecosystem properties of the respective sites.

Nevertheless, **a robust calibration of the BPCA to the HyPy method, like presented here would help to increase the representativity of global datasets including all methods, such as in chapter 1.** Yet, separate entities in landscapes have to be calibrated differently, thus it is important to have side information like land use, soil type, etc. To provide even better tools to correct and calibrate, it would be necessary to test the relationships in a larger variety of soils and environments. Since in this study climate conditions were the same for all samples it would be interesting to examine, if varying ecosystems also have an effect on the relationship between the two methods, similar to different matrixes.

Potential of DRIFT

DRIFT is a cheap tool, providing high throughput for the quantification and characterization of PyC. Such a tool could be extremely beneficial to acquire large databases of PyC (and potentially many more characterizations of SOC). **Here, the technique could reliably predict PyC_{BPCA} and PyC_{HyPy}, with always more than 80 % variance explained for HyPy and between 58 and 85 % variance explained for BPCA.** DRIFT has been used in previous studies to determine PyC using BPCA (Bornemann et al., 2008) or UV-Oxidation followed by NMR (Janik et al., 2007; Janik and Skjemstad, 1995; Jauss et al., 2015) as calibration, but never before including samples from forest floor or sediment. The advantage of DRIFT lies in its high throughput: more than 100 samples can be measured on one day, while other methods like BPCA or HyPy can provide not more than 20 to 25 samples per week and are very cost intensive. However, application and evaluation of the PLSR requires not only profound knowledge and experience of the statistical technique, but also a reasonably large training dataset, which should include > 50 samples. These training values need to be measured with another reliable method (e.g. HyPy) making it in any way necessary to also measure samples with the more labour and cost intensive methods. However, if a good training dataset exists, it can be used again and again for similar samples.

4.4 Decomposition vs. Stabilization of PyC

Using isotope labelling, most problems with the quantification of the relevant material disappear. Of course, this advantage applies only if artificially produced material is introduced as it is in this chapter. For the field experiments we thus have a very high precision for detecting our input grass and PyC material. This high precision allowed

us to detect not only very small differences in recovery of the inputs, but also robust calculations of the PEs.s

Bulk decomposition in different ecosystems

Figure 10 shows the recovery of initial input material in the three field sites. Focusing on the grass a clear latitudinal gradient is visible. Losses are highest in the tropical rainforest, followed by the temperate forest site. Decomposition is even much lower (highly significant) in the arctic site compared to the other two. These results are expected from the literature on SOC decomposition (Carvalhais et al., 2014; Chen et al., 2013; Heimann and Reichstein, 2008). Decomposition of PyC is much slower; or rather, losses of the initial input material are much smaller than for grass. This is also very much expected, since PyC features a much higher chemical recalcitrance and MRT than fresh organic input (Baldock and Smernik, 2002). However, if we look at the pattern of recovery in the varying ecosystems, it is striking to see, that the latitudinal gradient seen in the grass is not present for the PyC. **Losses of PyC input material are similarly low in the tropical and in the arctic site, but much higher in the temperate site. These results suggest, that there must be different mechanisms of decomposition and/or stabilization at work for grass and PyC.**

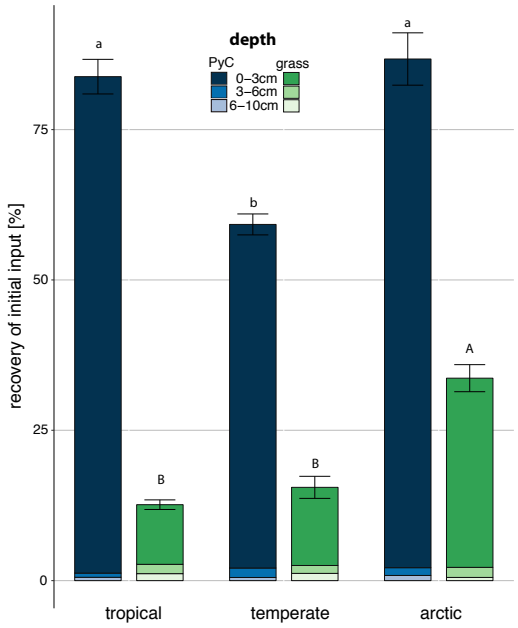


Figure 10: Recovery of initial input material per depth as % of the initial input. Bars represent standard errors and represent the bulk recovery. Small letters indicate significant differences of PyC input between sites and capital letters indicate significant differences of grass input between sites (p-value < 0.001). (Manuscript 4)

Vertical transport was generally rather low for both grass and PyC input (Figure 10). Only a few per cent of the initial input was recovered below 3 cm, indicating that the losses are probably not largely resulting from leaching or water transport (unless it is completely transported out of the mesocosm system). These values of vertical transport are in line with previous findings (Major et al., 2010; Singh et al., 2014).

Stabilization mechanisms

Density fractionation yielded interesting insights into the transformation of the two inputs (Figure 11). First, we noticed that in Siberia all the material was organic, meaning that no soil mineral phase was present in the first 3 cm. Therefore, all the recovered material could be attributed to the fLF, indicating that all the input recovered was still largely untransformed or unchanged after one year. In the other two ecosystems, transformation had already taken place and large parts of the initial input were found in aggregated form (oLF) or already associated to the mineral phase (HF), which generally also contains large parts of the microbial biomass. Thus, the values of still untransformed input indicated by the fLF are even much lower in the tropics and the temperate site. A striking highlight of Figure 11 is that we see the highest transformation – thus stabilization - in the place with the highest losses. **This feature could indicate, that a high initial decomposition could actually lead to a strong long-term storage, since the material is at the same time transformed to more stabilized forms.** At least we can clearly see that decomposition and stabilization are not opposite to each other, but rather drive each other and are linked interactively. These interactions are not well understood yet, and we showed for the first time empirically that they are probably varying largely between pyrogenic and labile carbon.

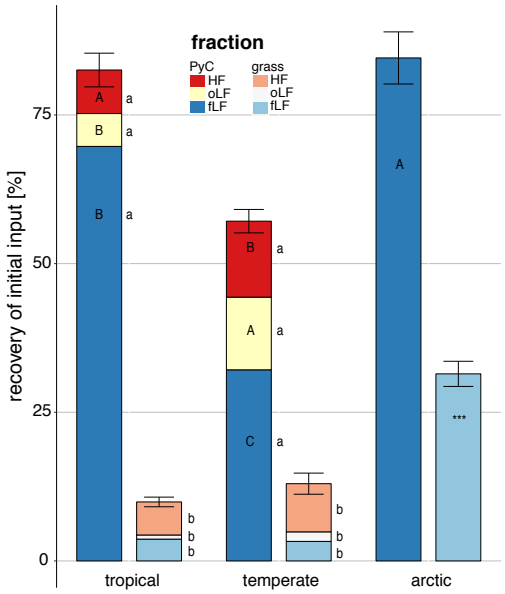


Figure 11: Recovery of initial input material as % of initial input in the density fractions. Bars represent standard errors and represent the bulk fractions, i.e. the recovery of the first horizon (0-3 cm). Small letters indicate significant differences between PyC and grass input within each site (p-value < 0.001), capital letters indicate significant differences of the PyC input between the sites (p-value < 0.05) and the asterisks indicate a significant difference between the grass recovery of Siberia and the other two sites (p-value < 0.001). (Manuscript 4)

Such differences could stem from a set of different processes and mechanisms. Physical breakdown or dislocation can play an important role and are most likely very different for PyC and fresh C forms. We could show that freeze-thawing and mechanical stress can lead to strong fragmentation in grass-PyC (Gmünder et al., in prep.). Other mechanisms, like bioturbation and microbial activity most likely also

play a crucial role. I speculate, that microbial communities in different ecosystems are not equally equipped to decompose PyC, since they are used to an organic input, which is very specific for their environment. Especially since we used a grass type, which originates from the temperate ecosystem, the special behaviour of the temperate site, might be explained by this fact. However, I could not find literature investigating such microbial decomposition processes, and in the scope of this thesis it was not possible to test it.

Site-specific drivers

With the site-specific drivers we wanted to investigate whether other environmental properties like the pH or water saturation might have an influence on the decomposition of grass and PyC. **Our results showed, however, no significant differences between the two treatments for any of the sites.** From the literature (as well as chapter 1 and 2), we would have expected that pH (tested at the temperate site) might have an influence on the decomposition and stabilization of PyC (Aciego Pietri and Brookes, 2008; Braadbaart et al., 2009; Kemmitt et al., 2006), contrarily this was not the case. Furthermore, the drought and the water table treatments in the tropical and the arctic site, respectively, showed no significant differences. These results were very surprising and we could not explain them.

Priming

It is on the one hand important for carbon dynamics to study the decomposition and stabilization behaviour of carbon input into the soil system, but on the other hand also how this affects the residual, native SOC. **Here we could show that the impact of grass and PyC on the native PyC was large in magnitude and extremely variable, for both bulk samples as well as density fraction thereof (**Figure 12**).** We found on average a negative PE on the temperate site, opposite to previous findings in the same place (Singh et al., 2014). In the tropical soil on the other hand, we found on average a positive PE. However, variation in the 14 replicates was usually much higher (even an order of magnitude) than the actual effect size. Furthermore, it is difficult at this point to explain how decomposition could decrease as much as to save more than 10 % of SOC stocks in one single year, compared to control samples. Our findings suggest that the underlying processes of priming are still poorly understood and need further investigation on different temporal (see also chapter 2) and spatial scales and in different ecosystems. Further

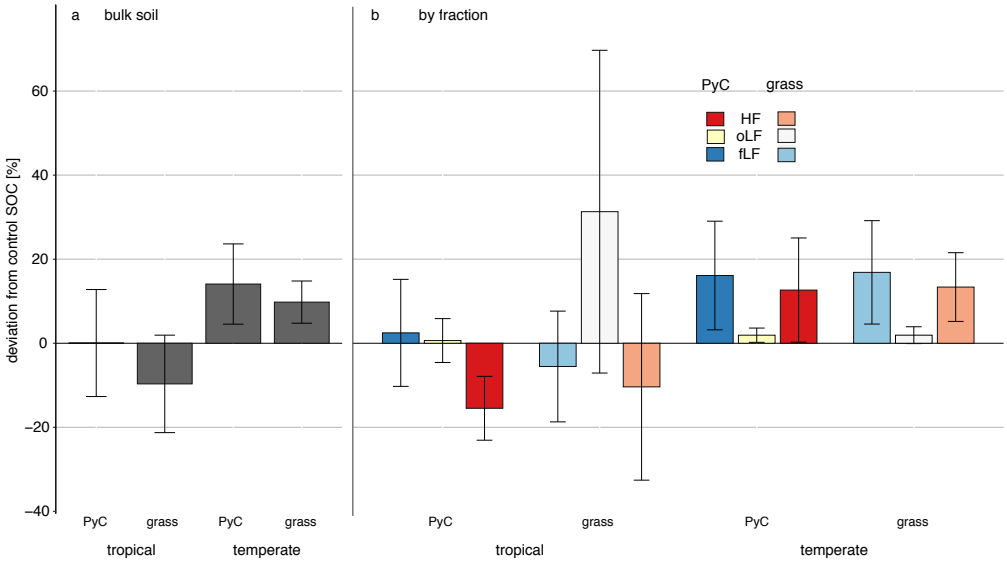


Figure 12: Priming effect in the tropical and temperate site shown as the relative change (%) of the SOC during the experiment for a) the bulk samples and b) the density fractions. Whiskers represent the standard error. (Manuscript 4)

investigations are crucial, if we just keep in mind, that a 10 % stock change of SOC is roughly 20 times more than the annual atmospheric carbon increase (IPCC, 2013).

5 Synthesis

"When you have eliminated the impossible, whatever remains, however improbable, must be the truth."

Sherlock Holmes - Arthur Conan Doyle

5.1 Summary and answer to the research questions

Global Distribution

1. **What are the PyC contents and stocks in different ecosystems?**
   Highest contents of PyC were found in soils with high clay content and high pH suggesting a higher importance of these factors than certain climatic conditions. PyC stocks are very much dependent on the present SOC stocks and are thus highest in ecosystems with very high SOC storage like the boreal and arctic regions.

2. **Which are the drivers explaining the distribution of PyC best?**
   Generally, soil properties like clay content and pH predict PyC contents much better than climate while fire cannot be used at least on a global level, however, locally fire seems to be an elemental predictor.

3. **Is it possible to create a model by using significant drivers of PyC contents to predict it on a global scale?**
   We could create a model to predict contents and stocks of PyC, which represents a first estimate of the global distribution.

Drivers of PyC Content and is Effect on SOC dynamics

1. **Which drivers explain the content/stocks of PyC in Swiss forests?**
   Soil properties represented by pH and clay content were again significant drivers of PyC contents. Climate was also an important predictor, however, here precipitation was correlated significantly with PyC contents while temperature was not.

2. **How does PyC relate to the dynamics of SOC?**
   There are clear relations between the PyC contents measured with the BPCA method and the turnover of SOC, even on long timescales.

3. **What is the relation between the results of the BPCA and the HyPy method?**
   There is a linear relationship between BPCA and HyPy, but the slope is approximately 0.21 with an intercept of 1.

Method comparison

1. **What is the relation between the results of the BPCA and the HyPy method?**
   The linear relationship between BPCA and HyPy was found to have a slope of 0.23 and an intercept of 0.05, being different from the results obtained in chapter 2.

2. **How is that relation different in different matrixes?**
   This relationship seems to vary between different environmental matrixes like sediments or for forest floor.

3. **Can DRIFT be used as a cheap and fast method to substitute for these methods?**
   DRIFT could reliably predict PyC contents in all matrixes when trained with either BPCA or HyPy.

Decomposition vs. Stabilization

1. **How fast do PyC and grass decompose in different ecosystems?**
   Grass decomposition followed a clear latitudinal gradient from tropical to arctic, however, PyC decomposition did not. PyC decomposition was highest at the temperate site.

2. **How are the two materials stabilized in aggregates and on mineral surfaces?**
   There was evidence for a strong stabilization of PyC in aggregates and on mineral surfaces, which was much less visible for the grass.

3. **What influence do the site-specific driver have on first two questions?**
   Site-specific differences did not have any effect on C dynamics, but only the differences between the sites and the inputs.

4. **What direction and magnitude is the priming under all these treatments?**
   Priming was found to be positive and negative and exhibiting very high variabilities and magnitudes.

5.2 Ranges and Variability of PyC contents across the studies

Measured PyC contents of SOC across the scales varied substantially. While the values ranged from 0 to 30 % of SOC in chapter 3 and from 0 to 10 % in chapter 2 (both forest soils; measured with HyPy), the global spread was 0 to 60 % with a mean at 13.7 % (all methods combined). From chapter 1, we could also determine the range of values for forest soils, which is 0 to 45 % from 116 measurements, however the mean is only 9.7 %. Therefore, the data seems largely comparable. The higher values in chapter 3, compared to chapter 2 can be explained by the recent fire activity in the area. The higher variability in the global dataset of chapter 1 can be explained by the comprehension of many different ecosystems (not only temperate forests, but also tropical and boreal forests) as well as many different methods.

5.3 Drivers and Processes on different temporal and spatial scales

Table 2 and 3 highlight the found relations between different drivers of PyC contents and their influence on spatial scales, as well as processes related to these contents on different temporal scales. Question marks indicate gaps of knowledge, where we still do not have sufficient data available. There is an apparent pattern, which can be observed from the table. **On one hand, there are a lot of gaps on drivers of PyC content on smaller spatial scales such as landscapes or even fields. On the other hand, for most of the processes it is very difficult to estimate the influence on long temporal scales.**

Drivers

Climatic drivers often have been the first to be compared to SOC or PyC stocks (Cheng et al., 2008; Glaser and Amelung, 2003; Jauss et al., 2015). **The results from the four chapters, however, show evidence that temperature and precipitation act differently on varying scales.** Our results strongly suggest that up- or downscaling of climatic drivers is hardly possibly from single studies. The reason for the differences between the scales for precipitation and temperature is not clear, but similar patterns exist for the bulk SOC.

Table 2: Summary of the drivers and their influence at different spatial scales. Cells marked with x are covered in the chapters of this thesis. If other studies found a relationship, which is not covered by this thesis, a reference is given. If no reference could be found, the cell is highlighted with a question mark.

	spatial scale			
	local	landscape	country	global
Drivers of PyC content				
Temperature	?	?	x	x
Precipitation	?	?	x	x
pH	x	?	x	x
clay content	?	?	x	x
landform	(Rumpel et al., 2006)	(Cotrufo et al., 2016)	x	?
fire activity	(Ansley et al., 2006)	x	x	x

influence

- none
- small
- significant
- highly significant

Studies on the interaction between SOC and climatic drivers also found that temperature is significantly related on global scales, while precipitation is significantly related on smaller scales like landscape or even local (Davidson and Janssens, 2006; Doetterl et al., 2015; Giardina et al., 2014; Jung et al., 2017; Moyano et al., 2012).

Recent literature shows that there might be a so-called “legacy effect” of microbial communities with soil moisture, i.e. microbial communities react differently on soil moisture, depending on what they were exposed to (Hawkes et al., 2017). Such a “legacy effect” would be more pronounced on smaller scales, offering a possible explanation, why precipitation is a more significant driver there. However, how this is all linked to PyC content is very difficult to disentangle and deserves further attention and investigation.

When it comes to soil properties like clay content and pH, the knowledge about relations with PyC content are becoming more and more clear, as there exists an increasing amount of literature on this topic on large environmental gradients and spatial scales (Cusack et al., 2012; Jauss et al., 2015; Lehmann et al., 2015). What is lacking are studies on smaller scales. **Chapter 4 showed the surprising result, that pH did not have an effect on the PyC content in two soils right next to each other, while the global inventory in chapter 1 found a very clear and highly significant correlation** (also in the pH ranges of the examined soils in chapter 4)**.** Before these results, one would usually have assumed that soil properties are equally important on all scales, but the story seems to be much more complicated.

Chapter 2 has shown that landform and fire activity did not have an impact on the PyC content, at least if the fires had already happened long time ago (decades or centuries). Even though it has been shown that PyC can be eroded preferentially compared to other SOC (Cotrufo et al., 2016; Rumpel et al., 2006), such a process would probably be on short timescales, when the deposited PyC is still on top of the soil surface (see Table 2). **Therefore, both drivers - fire activity and landform - are very important on short temporal scales, but lose importance, the longer ago the fire and subsequent deposition of PyC happened.** The reason why fire plays such a minor role on large spatial scales is however different. Here, it is mainly a problem of resolution, because global fire datasets are derived from not more than the last two decades and spatial resolution is usually too low to capture the spatial heterogeneity of fires.

This problem of changing drivers and variables, with changing applied resolution is known as the modifiable area unit problem and has implications all over geography (Openshaw, 1983). **Thus, some of the differences between the different spatial scales might simply be traced back to this statistical problem.** It remains important to keep this in mind for comparing results between studies on different scales as well as for up- or downscaling and modelling approaches.

Processes

It is apparent from Table 3 that most processes are very important on short temporal scales. Deposition and (preferential) erosion are both most prominent very shortly after a fire happened. Direct deposition (being produced on the soil surface or falling down on it) is immediate, while transport by air can delay the time of deposition by not more than several days (Bowman et al., 2009). Erosion happens mostly during the time after a fire, when the PyC is not incorporated into the mineral soil and can be easily flushed by rain (Cotrufo et al., 2016; Rumpel et al., 2006). Here fragmentation comes in as a very important linking process, because physical breakdown only enables effective transport of PyC into deeper soil layers.

Table 3: Influence of Processes on varying timescales. Cells marked with x are covered in the chapters of this thesis. If other studies found a relationship, which is not covered by this thesis, a reference is given. If no reference could be found, the cell is highlighted with a question mark.

	temporal scale			
	> 100 years	> 10 years	> 1 month	< 1 month
Processes				
Deposition	(Bowman et al., 2009)	(Bowman et al., 2009)	(Bowman et al., 2009)	x
Erosion	?	?	(Cotrufo et al., 2016)	(Rumpel et al., 2006)
Fragmentation	?	?	x	x
Priming Effect	x	x	x	(Maestrini et al., 2014b)
Aggregation	(Brodowski et al., 2006)	(Brodowski et al., 2006)	x	(Lehmann et al., 2009)
Mineral Interaction	(Lehmann et al., 2015)	(Lehmann et al., 2015)	x	(Santos et al., 2012)
Microbial Decomposition	?	?	(Santos et al., 2012)	(Santos et al., 2012)

influence

- none
- small
- significant
- highly significant

The importance of fragmentation in the preservation and loss of PyC is likely very high and has probably been underestimated in previous studies on PyC (Spokas et al., 2014). It is therefore also not surprising, that little data exists of fragmentation on longer timescales than a year. The PE has also always been mainly investigated over short timescales. One reason for this is that the additions of C were usually also materials with low MRT in soil, like glucose (Kuzyakov et al., 2000), which then also would not lead to a long lasting PE.

Only recently the focus has also changed on the PE of PyC, mainly in the form of biochar (Ahn et al., 2011; Maestrini et al., 2014b; Singh et al., 2014). **However, even for PyC the longest PE measured was not more than 3 years (Maestrini et al., 2014b) and statements that PyC might feature a very long PE of more than a decade are only based on speculations (Woolf and Lehmann, 2012). Here we could fill this gap and show strong priming over the first year (chapter 4) and that PyC is influencing SOC turnover on timescales of centuries, even if we could not strictly define our findings as PE (chapter 2).** Magnitudes and variability were much higher in chapter 4, indicating a flattening out of the PE the longer it lasts.

Stabilization mechanisms like mineral binding or complexation and aggregation might be processes, which take place on relatively short temporal scales, however the consequences of these processes, namely the stabilization of PyC last much longer (Lehmann et al., 2009). This is illustrated by the evidence, that PyC was strongly stabilized in European black soils in aggregates and on mineral surfaces even after centuries (Brodowski et al., 2006). Our results in chapter 4 also provided evidence, that a strong transformation in the first year after input leads to an equally strong stabilization of PyC in the aggregated and mineral associated forms.

To sum it up, it becomes clearer that it is the short events and processes, which shape the long-term effects of PyC through fires, erosion, decomposition and stabilization. Since short and heavy events like fires and heavy rains are supposed to increase with global change (IPCC, 2013), this might also have very strong implications for the persistence of PyC and C in general in the soil system.

6 Limitations and Perspectives

Besides the new and interesting findings, this work poses many challenges, to be overcome in the future,. But it also raises many new questions on drivers of decomposition, stabilization and priming on varying scales, their importance in different ecosystems and landscapes and their underlying principles. This thesis is thus only like a piece of a whole puzzle. There are several limitations to this work and past work in general, which need to be overcome, when looking for the missing pieces.

The global dataset from chapter 1 is spatially very unbalanced and is in great need for data from yet poorly or unexplored regions. Furthermore, the variety of methods hampers robust comparability (see chapter 6.1). We are still limited to a set of different quantification methods, of which none can yet quantify the whole continuum of PyC reliably. DRIFT could be a way to go, but it needs some efforts to be a successful tool in the future (see chapter 6.2). What also remains unclear is, if decomposition and stabilization in soils are enough to explain the fate of PyC after its decomposition. The proposed “pre-ageing” of PyC before it reaches the oceans poses more challenges and demands for new approaches (chapter 6.3).

Moreover, the most fundamental driver of decomposition, the soil microbial community, was not investigated at all in any of the chapters. We even found evidence that abiotic processes like fragmentation might be equally or even more important. It will be very critical to further investigate the relations between abiotic and biotic degradation of PyC (see chapter 6.4).

6.1 Unification and Comparability

As seen from Figure 9, the highest stocks of PyC are probably found in very high latitudes as well as tropical ecosystems. However, these are exactly the places, where least of published PyC data of chapter 1 come from. This mismatch between high stocks and research areas leads to a strong bias in our understanding of PyC in soils. **To improve global estimations and drivers it is absolutely elemental to balance out these heterogeneities by including the areas of the world where yet few studies exist in current research.** This thesis also showed, that scaling is an important factor for the comparability of results and needs to be taken into account in future modelling approaches and comparative analyses. Furthermore, it is apparent and well known that the quantification methods of PyC are not directly comparable. Even though they yield values in similar ranges

when looking at the global picture. **Our results from chapters 2 and 3 suggest that we need to unify these methods and should use the best fitting one according to respective research question**. Most of the methods in use (except DRIFT) are labour and cost intensive, while being limited in information on PyC quality and/or quantity.

6.2 DRIFT and machine learning

Being cheap and fast at the same time, DRIFT is potentially the only method to overcome the above-mentioned limitations, . It was proven as a powerful tool, when quantifying and characterizing PyC and other soil related variables with very large sample numbers. PLSR basically represents a machine learning process, where a training set of soils is used to calibrate a model, which can then predict values in other soils, based on what the model learnt from the training. To effectively train such a model, a large dataset is required, which covers the full range of expected variables in it. **When such large training datasets are established, huge databases could be acquired, which exceed the ones produced with BPCA, HyPy or other methods easily by one order of magnitude.**

This is an advantage and disadvantage at the same time, since it not only answers questions on large spatial scales as well as with high resolution, but also requires always a large enough training dataset. The training dataset needs to be measured with an alternative method, which is then cost and labour extensive again. **Therefore, DRIFT requires an initial investment, which should not be underestimated. Such an investment would require international collaboration and networks, and an open data sharing policy.** Without a stronger consensus on methods and practices it will be very difficult to push the understanding of PyC in the environment to the next level.

6.3 From soil to sea – missing links?

This whole work has tried to illuminate various aspects of PyC in soils. But concerning topics like the long-term storage of carbon (climate mitigation), stabilization in the ecosystem and actual pathways of the PyC, it is crucial to also look at other environments than just soils. When PyC enters the ocean at the river mouths of Amazon, Mississippi or other big rivers, it features in average already ages of several thousand years (Coppola et. al, in rev.; Masiello and Druffel, 1998). At the same time, the turnover time of PyC in soils is usually somewhere between 100 and 1000 years (Lehmann and Joseph, 2015; Singh et al., 2012; Zimmermann et al.,

2012). **Therefore, PyC cannot uniquely be stored in soils, because then it should theoretically feature ages of not much more than 1000 years, when eroded to the sea.** Hence the question: where did the carbon stay all that time (or "pre-age"), until it reached the sea? There must apparently be intermediate pools, where PyC is stored and stabilized on longer terms than in average soils. These could be river sediments, the rocks below soil, or in specific soils, which lie in certain landforms like depressions, supporting stabilization. Another very general question, which is also loosely tied to the above mentioned problem is, whether it is actually a benefit for the PyC to reside in the soil, if long-term stabilization is targeted. **Since MRTs of PyC in marine sediments trend towards geological timescales, it might actually be profitable to enable quick transport to the ocean.** A more holistic earth-systems view on the topic of PyC might enable us to understand and predict its pathways and feedbacks much better.

6.4 Biotic vs. Abiotic Processes

Basically all mineralization and decomposition is happening through the activity of microorganism even though actually only a tiny part of SOC is microbial biomass (Brookes, 2001). Or formulated differently microbial biomass is *"the eye of the needle through which all organic matter must pass"* when transformed and decomposed (Jenkinson, 1977). However, it is unclear to which degree this paradigm also holds true for PyC. Recent studies suggest, that abiotic processes could be very important for PyC mineralization, mainly UV or chemical oxidation (Cheng et al., 2006; Zimmerman et al., 2010) or reburning in very fire prone ecosystems (Saiz et al., 2014). Additionally, our findings in chapter 4 and from a master thesis (Gmünder et al. in prep.) suggest, that physical processes like fragmentation could be very important.

There is also evidence that PyC has a variety of important effects on other biotic processes, through e.g. the release of toxic compounds, creation of habitat through pore space, formation of aggregates or the absorption of important compounds like nutrients, enzymes or second messengers (LeCroy et al., 2013; Lehmann et al., 2011; Masiello et al., 2013).

To disentangle these biotic and abiotic process, new ways and approaches have to be taken. Elaborate labelling and/or the use of genetically modified microorganisms might provide a tool to achieve this. All chapters in this thesis could potentially benefit from additional information on this complex relation of biotic and abiotic processes.

References

Abiven, S., and Andreoli, R. (2010). Charcoal does not change the decomposition rate of mixed litters in a mineral cambisol: a controlled conditions study. *Biol. Fertil. Soils* 47, 111–114. doi:10.1007/s00374-010-0489-1.

Abiven, S., Hengartner, P., Schneider, M. P. W., Singh, N., and Schmidt, M. W. I. (2011). Pyrogenic carbon soluble fraction is larger and more aromatic in aged charcoal than in fresh charcoal. *Soil Biol. Biochem.* 43, 1615–1617. doi:10.1016/j.soilbio.2011.03.027.

Aciego Pietri, J. C., and Brookes, P. C. (2008). Relationships between soil pH and microbial properties in a UK arable soil. *Soil Biol. Biochem.* 40, 1856–1861. doi:10.1016/j.soilbio.2008.03.020.

Ahn, M.-Y., Zimmerman, A. R., Gao, B., and Ahn, M.-Y. (2011). Positive and negative carbon mineralization priming effects among a variety of biochar-amended soils. *Soil Biol. Biochem.* 43, 1169–1179. doi:10.1016/j.soilbio.2011.02.005.

Amelung, W., Brodowski, S., Sandhage-Hofmann, A., and Bol, R. (2008). “Chapter 6 Combining Biomarker with Stable Isotope Analyses for Assessing the Transformation and Turnover of Soil Organic Matter,” in Advances in Agronomy. (Academic Press), 155–250. doi:https://doi.org/10.1016/S0065-2113(08)00606-8.

Ansley, R. J., Boutton, T. W., and Skjemstad, J. O. (2006). Soil organic carbon and black carbon storage and dynamics under different fire regimes in temperate mixed-grass savanna. *Global Biogeochem. Cycles* 20. doi:10.1029/2005GB002670.

Archibald, S., Lehmann, C. E. R., Gómez-dans, J. L., and Bradstock, R. A. (2013). Defining pyromes and global syndromes of fire regimes. *Proc. Natl. Acad. Sci. U. S. A.* 110, 6442–6447. doi:10.1073/pnas.1211466110/-/DCSupplemental.www.pnas.org/cgi/doi/10.1073/pnas.1211466110.

Ascough, P. L., Bird, M. I., Brock, F., Higham, T. F. G., Meredith, W., Snape, C. E., et al. (2009). Hydropyrolysis as a new tool for radiocarbon pre-treatment and the quantification of black carbon. *Quat. Geochronol.* 4, 140–147. doi:10.1016/j.quageo.2008.11.001.

Ascough, P. L., Bird, M. I., Francis, S. M., Thornton, B., Midwood, a. J., Scott, a. C., et al. (2011). Variability in oxidative degradation of charcoal: Influence of

production conditions and environmental exposure. *Geochim. Cosmochim. Acta* 75, 2361–2378. doi:10.1016/j.gca.2011.02.002.

Baldock, J. A., and Smernik, R. J. (2002). Chemical composition and bioavailability of thermally altered Pinus resinosa (Red pine) wood. *Org. Geochem.* 33, 1093–1109. doi:10.1016/S0146-6380(02)00062-1.

Barker, T. (2007). Climate Change 2007 : An Assessment of the Intergovernmental Panel on Climate Change. *Change* 446, 12–17. doi:10.1256/004316502320517344.

Beringer, J., Hutley, L. B., Tapper, N. J., and Cernusak, L. a. (2007). Savanna fires and their impact on net ecosystem productivity in North Australia. *Glob. Chang. Biol.* 13, 990–1004. doi:10.1111/j.1365-2486.2007.01334.x.

Bingeman, C. W., Varner, J. E., and Martin, W. P. (1953). The Effect of the Addition of Organic Materials on the Decomposition of an Organic Soil. *Soil Sci. Soc. Am. J.* 17, 34–38. doi:10.2136/sssaj1953.03615995001700010008x.

Bird, M. I., Moyo, C., Veenendaal, E. M., Lloyd, J., and Frost, P. (1999). Stability of elemental carbon in a savanna soil. *Geoderma* 13, 923–932.

Bird, M. I., Wynn, J. G., Saiz, G., Wurster, C. M., and McBeath, A. (2015). The Pyrogenic Carbon Cycle. *Annu. Rev. Earth Planet. Sci.* 43, 273–98. doi:10.1146/annurev-earth-060614-105038.

Bond, T. C., Doherty, S. J., Fahey, D. W., Forster, P. M., Berntsen, T., Deangelo, B. J., et al. (2013). Bounding the role of black carbon in the climate system: A scientific assessment. *J. Geophys. Res. Atmos.* 118, 5380–5552. doi:10.1002/jgrd.50171.

Boot, C. M., Haddix, M., Paustian, K., and Cotrufo, M. F. (2015). Distribution of black carbon in ponderosa pine forest floor and soils following the High Park wildfire. *Biogeosciences* 12, 3029–3039. doi:10.5194/bg-12-3029-2015.

Bornemann, L., Welp, G., Brodowski, S., Rodionov, A., and Amelung, W. (2008). Rapid assessment of black carbon in soil organic matter using mid-infrared spectroscopy. *Org. Geochem.* 39, 1537–1544. doi:10.1016/j.orggeochem.2008.07.012.

Bowman, D. M. J. S., Balch, J. K., Artaxo, P., Bond, W. J., Carlson, J. M., Cochrane, M. A., et al. (2009). Fire in the Earth System. *Science.* 324, 481–484. doi:10.1126/science.1163886.

Braadbaart, F., Poole, I., and van Brussel, A. A. (2009). Preservation potential of charcoal in alkaline environments: an experimental approach and implications

for the archaeological record. *J. Archaeol. Sci.* 36, 1672–1679. doi:10.1016/j.jas.2009.03.006.

Brodowski, S., John, B., Flessa, H., and Amelung, W. (2006). Aggregate-occluded black carbon in soil. *Eur. J. Soil Sci.* 57, 539–546. doi:10.1111/j.1365-2389.2006.00807.x.

Brookes, P. (2001). The Soil Microbial Biomass: Concept, Measurement and Applications in Soil Ecosystem Research. *Microbes Environ.* 16, 131–140. doi:10.1264/jsme2.2001.131.

Bucheli, T. D., Blum, F., Desaules, A., and Gustafsson, O. (2004). Polycyclic aromatic hydrocarbons, black carbon, and molecular markers in soils of Switzerland. *Chemosphere* 56, 1061–76. doi:10.1016/j.chemosphere.2004.06.002.

Carvalhais, N., Forkel, M., Khomik, M., Bellarby, J., Jung, M., Migliavacca, M., et al. (2014). Global covariation of carbon turnover times with climate in terrestrial ecosystems. *Nature* 514, 213–217. doi:10.1038/nature13731.

Chen, S., Huang, Y., Zou, J., and Shi, Y. (2013). Mean residence time of global topsoil organic carbon depends on temperature, precipitation and soil nitrogen. *Glob. Planet. Change* 100, 99–108. doi:10.1016/j.gloplacha.2012.10.006.

Cheng, C. H., Lehmann, J., Thies, J. E., and Burton, S. D. (2008). Stability of black carbon in soils across a climatic gradient. *J. Geophys. Res. Biogeosciences* 113, 1–10. doi:10.1029/2007JG000642.

Cheng, C. H., Lehmann, J., Thies, J. E., Burton, S. D., and Engelhard, M. H. (2006). Oxidation of black carbon by biotic and abiotic processes. *Org. Geochem.* 37, 1477–1488. doi:10.1016/j.orggeochem.2006.06.022.

Chuvieco, E., Giglio, L., and Justice, C. (2008). Global characterization of fire activity: toward defining fire regimes from Earth observation data. *Glob. Chang. Biol.* 14, 1488–1502. doi:10.1111/j.1365-2486.2008.01585.x.

Cotrufo, M. F., Boot, C. M., Kampf, S., Nelson, P. A., Brogan, D. J., Covino, T., et al. (2016). Redistribution of pyrogenic carbon from hillslopes to stream corridors following a large montane wildfire. *Global Biogeochem. Cycles* 30, 1348–1355. doi:10.1002/2016GB005467.Received.

Cross, A., and Sohi, S. P. (2011). The priming potential of biochar products in relation to labile carbon contents and soil organic matter status. *Soil Biol. Biochem.* 43, 2127–2134. doi:10.1016/j.soilbio.2011.06.016.

Cusack, D. F., Chadwick, O. A., Hockaday, W. C., and Vitousek, P. M. (2012).

Mineralogical controls on soil black carbon preservation. *Global Biogeochem. Cycles* 26, 1–10. doi:10.1029/2011GB004109.

Davidson, E. A., and Janssens, I. A. (2006). Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. *Nature* 440, 165–173. doi:10.1038/nature04514.

Dinel, H., Schnitzer, M., and Meyhuys, G. R. (1990). *Soil lipids: origin, nature, content, decomposition, and effect on soil physical properties.* Sixth Edit. , eds. J. M. Bollag and G. Stotzky New York: Marcel Dekker Inc.

Doetterl, S., Stevens, A., Six, J., Merckx, R., Van Oost, K., Casanova Pinto, M., et al. (2015). Soil carbon storage controlled by interactions between geochemistry and climate. *Nat. Geosci.* 8, 780–783. doi:10.1038/ngeo2516.

Edwards, A. P., and Bremner, J. M. (1967). Microaggregates in soils. *J. Soil Sci.* 18, 64–73. doi:10.1111/j.1365-2389.1967.tb01488.x.

FAO/IIASA/ISRIC/ISSCAS/JRC (2012). Harmonized World Soil Database (version 1.2).

Forbes, M. S., Raison, R. J., and Skjemstad, J. O. (2006). Formation, transformation and transport of black carbon (charcoal) in terrestrial and aquatic ecosystems. *Sci. Total Environ.* 370, 190–206. doi:10.1016/j.scitotenv.2006.06.007.

Friedl, M. A., Sulla-Menashe, D., Tan, B., Schneider, A., Ramankutty, N., Sibley, A., et al. (2010). MODIS Collection 5 global land cover: Algorithm refinements and characterization of new datasets. *Remote Sens. Environ.* 114, 168–182. doi:10.1016/j.rse.2009.08.016.

Gelinas, Y., Kenneth, M., Baldock, J. A., and Hedges, J. I. (2001). An Improved Thermal Oxidation Method for the Quantification of Soot / Graphitic Black Carbon in Sediments and Soils. *Environ. Sci. Technol.* 35, 3519–3525. doi:10.1021/es010504c.

Giardina, C. P., Litton, C. M., Crow, S. E., and Asner, G. P. (2014). Warming-related increases in soil CO2 efflux are explained by increased below-ground carbon flux. *Nat. Clim. Chang.* 4, 822–827. doi:10.1038/nclimate2322.

Giglio, L., Randerson, J. T., and Van Der Werf, G. R. (2013). Analysis of daily, monthly, and annual burned area using the fourth-generation global fire emissions database (GFED4). *J. Geophys. Res. Biogeosciences* 118, 317–328. doi:10.1002/jgrg.20042.

Glaser, B., and Amelung, W. (2003). Pyrogenic carbon in native grassland soils along a climosequence in North America. *Global Biogeochem. Cycles* 17.

doi:10.1029/2002GB002019.

Glaser, B., Haumaier, L., Guggenberger, G., and Zech, W. (1998). Black carbon in soils : the use of benzenecarboxylic acids as specific markers. *Org. Geochem.* 29, 811–819.

Goldberg, E. D. (1985). Black Carbon in the Environment. *Q. J. R. Meteorol. Soc.* 112, 563–564. doi:10.1002/qj.49711247219.

Güereña, D. T., Lehmann, J., Walter, T., Enders, A., Neufeldt, H., Odiwour, H., et al. (2015). Terrestrial pyrogenic carbon export to fluvial ecosystems: Lessons learned from the White Nile watershed of East Africa. *Global Biogeochem. Cycles* 29, 1911–1928. doi:10.1002/2015GB005095.Received.

Guggenberger, G., Rodionov, A., Shibistova, O., Grabe, M., Kasansky, O. a., Fuchs, H., et al. (2008). Storage and mobility of black carbon in permafrost soils of the forest tundra ecotone in Northern Siberia. *Glob. Chang. Biol.* 14, 1367–1381. doi:10.1111/j.1365-2486.2008.01568.x.

Guo, Y., and Bustin, R. M. (1998). FTIR spectroscopy and reflectance of modern charcoals and fungal decayed woods: implications for studies of inertinite in coals. *Int. J. Coal Geol.* 37, 29–53. doi:10.1016/S0166-5162(98)00019-6.

Gustafsson, O., Bucheli, D., Kukulska, Z., Andersson, M., Largeau, C., Rouzaud, J.-N., et al. (2001). Evaluation of a protocol for the quantification of black carbon in sediments. *Global Biogeochem. Cycles* 15, 881–890.

Gustafsson, O., Haghseta, F., Chan, C., Macfarlane, J., and Gschwend, P. M. (1997). Quantification of the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability. *Environ. Sci. Technol.* 31, 203–209. doi:10.1021/es960317s.

Hammes, K., and Abiven, S. (2013). “Identification of Black Carbon in the Earth System,” in *Fire Phenomena and the Earth System*, ed. C. Belcher (West Sussex: John Wiley & Sons), 157–176. doi:10.1002/9781118529539.ch9.

Hammes, K., Schmidt, M. W. I., Smernik, R. J., Currie, L. a., Ball, W. P., Nguyen, T. H., et al. (2007). Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere. *Global Biogeochem. Cycles* 21. doi:10.1029/2006GB002914.

Hanke, U. M., Reddy, C. M., Braun, A. L. L., Coppola, A., Haghipour, N., McIntyre, C. P., et al. (2017). What on Earth have we been burning? Deciphering sedimentary records of pyrogenic carbon. *Environ. Sci. Technol.* 51, 12972–

12980. doi:10.1021/acs.est.7b03243.

Hart, S. A., and Luckai, N. J. (2014). Charcoal carbon pool in North American boreal forests. *Ecosphere* 5. doi:10.1890/ES13-00086.1.

Hassink, J. (1997). The capacity of soils to preserve organic C and N by their association with clay and silt particles. *Plant Soil* 191, 77–87. doi:10.1023/A:1004213929699.

Hawkes, C. V., Waring, B. G., Rocca, J. D., and Kivlin, S. N. (2017). Historical climate controls soil respiration responses to current soil moisture. *Proc. Natl. Acad. Sci.* 114, 6322–6327. doi:10.1073/pnas.1620811114.

Hedges, J. I., Eglinton, G., Hatcher, P. G., Kirchman, D. L., Arnosti, C., Derenne, S., et al. (2000). The molecularly uncharacter ized component of nonliving organic matter in natural environments. *Org. Geochem.* 31, 945–958. doi:http://dx.doi.org/10.1016/S0146-6380(00)00096-6.

Heimann, M., and Reichstein, M. (2008). Terrestrial ecosystem carbon dynamics and climate feedbacks. *Nature* 451, 289–292. doi:10.1038/nature06591.

Hockaday, W. C., Grannas, A. M., Kim, S., and Hatcher, P. G. (2007). The transformation and mobility of charcoal in a fire-impacted watershed. *Geochim. Cosmochim. Acta* 71, 3432–3445. doi:10.1016/j.gca.2007.02.023.

IPCC (2013). Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge.

Jaffe, R., Ding, Y., Niggemann, J., Vahatalo, A. V., Stubbins, A., Spencer, R. G. M., et al. (2013). Global Charcoal Mobilization from Soils via Dissolution and Riverine Transport to the Oceans. *Science.* 340, 345–347. doi:10.1126/science.1231476.

Janik, L. J., and Skjemstad, J. O. (1995). Characterization and analysis of soils using mid-infrared partial least-squares. II. Correlations with some laboratory data. *Aust. J. Soil Res.* 33, 637–650. doi:10.1071/SR9950637.

Janik, L. J., Skjemstad, J. O., Shepherd, K. D., and Spouncer, L. R. (2007). The prediction of soil carbon fractions using mid-infrared-partial least square analysis. *Soil Res.* 45, 73–81. Available at: https://doi.org/10.1071/SR06083.

Jauss, V., Johnson, M., Krull, E., Daub, M., and Lehmann, J. (2015). Pyrogenic carbon controls across a soil catena in the Pacific Northwest. *Catena* 124, 53–59. doi:10.1016/j.catena.2014.09.001.

Jenkinson, D. S. (1977). The soil biomass. *New Zeal. Soil News* 25, 213–218.

Jung, M., Reichstein, M., Schwalm, C. R., Huntingford, C., Sitch, S., Ahlström, A., et al. (2017). Compensatory water effects link yearly global land CO2 sink changes to temperature. *Nature* 541, 516–520. doi:10.1038/nature20780.

Keeling, R. F., Walker, S. J., Piper, S. C., and Bollenbacher, A. F. (2017). Atmospheric CO2 Concentrations (ppm) Derived from in Situ Air Measurements at Mauna Loa, Observatory, Hawaii. *Scripps CO2 Progr.* Available at: https://scripps.ucsd.edu/programs/keelingcurve/ [Accessed October 4, 2017].

Kemmitt, S. J., Wright, D., Goulding, K. W. T., and Jones, D. L. (2006). pH regulation of carbon and nitrogen dynamics in two agricultural soils. *Soil Biol. Biochem.* 38, 898–911. doi:10.1016/j.soilbio.2005.08.006.

Knicker, H. (2007). How does fire affect the nature and stability of soil organic nitrogen and carbon? A review. *Biogeochemistry* 85, 91–118. doi:10.1007/s10533-007-9104-4.

Knicker, H., Wiesmeier, M., and Dick, D. P. (2008). A simplified method for the quantification of pyrogenic organic matter in grassland soils via chemical oxidation. *Geoderma* 147, 69–74. doi:10.1016/j.geoderma.2008.07.008.

Kuhlbusch, T. A. J., Andreae, M. O., Cachier, H., Goldammer, J. G., Lacaux, J., Shea, R., et al. (1996). Black carbon formation by savanna fires : Measurements and implications for the global carbon cycle. *J. Geophys. Res.* 101, 23651–23665.

Kuzyakov, Y., Friedel, J. K., and Stahr, K. (2000). Review of mechanisms and quantification of priming effects. *Soil Biol. Biochem.* 32, 1485–1498. doi:10.1016/S0038-0717(00)00084-5.

Kuzyakov, Y., Subbotina, I., Chen, H., Bogomolova, I., and Xu, X. (2009). Black carbon decomposition and incorporation into soil microbial biomass estimated by 14C labeling. *Soil Biol. Biochem.* 41, 210–219. doi:10.1016/j.soilbio.2008.10.016.

LeCroy, C., Masiello, C. A., Rudgers, J. A., Hockaday, W. C., and Silberg, J. J. (2013). Nitrogen, biochar, and mycorrhizae: Alteration of the symbiosis and oxidation of the char surface. *Soil Biol. Biochem.* 58, 248–254. doi:10.1016/j.soilbio.2012.11.023.

Lehmann, J. (2007). Bio-energy in the black. *Front. Ecol. Environ.* 5, 381–387. doi:10.1890/1540-9295(2007)5[381:BITB]2.0.CO;2.

Lehmann, J., Abiven, S., Kleber, M., Pan, G., Singh, B. P., Sohi, S. P., et al. (2015). “Persistence of biochar in soil,” in *Biochar for Environmental Management* -

Science, Technology and Implementation, eds. J. Lehmann and S. Joseph (Sterlink, UK: Routledge), 235–282.

Lehmann, J., Czimczik, C. I., Laird, D., and Sohi, S. (2009). "Stability of Biochar in the Soil," in *Biochar for Environmental Management - Science and Technology*, eds. J. Lehmann and S. Joseph (Sterling, UK: earthscan), 189.

Lehmann, J., and Joseph, S. (2015). *Biochar for Environmental Management - Science, Technology and Implementation*. Second Edi. London: Routledge.

Lehmann, J., Kinyangi, J., and Solomon, D. (2007). Organic matter stabilization in soil microaggregates: Implications from spatial heterogeneity of organic carbon contents and carbon forms. *Biogeochemistry* 85, 45–57. doi:10.1007/s10533-007-9105-3.

Lehmann, J., Rillig, M. C., Thies, J., Masiello, C. A., Hockaday, W. C., and Crowley, D. (2011). Biochar effects on soil biota - A review. *Soil Biol. Biochem.* 43, 1812–1836. doi:10.1016/j.soilbio.2011.04.022.

Lehmann, J., Skjemstad, J., Sohi, S., Carter, J., Barson, M., Falloon, P., et al. (2008). Australian climate–carbon cycle feedback reduced by soil black carbon. *Nat. Geosci.* 1, 832–835.

Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., et al. (2006). Black Carbon Increases Cation Exchange Capacity in Soils. *Soil Sci. Soc. Am. J.* 70, 1719. doi:10.2136/sssaj2005.0383.

Lide, D. R. (2017). "Properties of Elements and Inorganic Compounds," in *CRC Handbook of Chemistry and Physics*, ed. D. R. Lide (Boca Raton, FL, USA: CRC Press/Taylor and Francis), 4–135.

Love, D., Snape, C. E., Carr, A. D., Houghton, C., and September, I. (1996). Release of covalently-bound alkane biomarkers in high yields from kerogen via catalytic hydropyrolysis. *Org. Geochem.* 23, 981–986.

Lowe, L. E. (1978). "Carbohydrates in soil," in *Soil Organic Matter*, eds. M. Schnitzer and S. U. Khan (Amsterdam: Elsevier), 65–93.

Luo, Y., Durenkamp, M., De Nobili, M., Lin, Q., and Brookes, P. C. (2011). Short term soil priming effects and the mineralisation of biochar following its incorporation to soils of different pH. *Soil Biol. Biochem.* 43, 2304–2314. doi:10.1016/j.soilbio.2011.07.020.

Macías, F., and Arbestain, M. C. (2010). Soil carbon sequestration in a changing global environment. *Mitig. Adapt. Strateg. Glob. Chang.* 15, 511–529. doi:10.1007/s11027-010-9231-4.

Maestrini, B., Abiven, S., Singh, N., Bird, J., Torn, M. S., and Schmidt, M. W. I. (2014a). Carbon losses from pyrolysed and original wood in a forest soil under natural and increased N deposition. *Biogeosciences* 11, 5199–5213. doi:10.5194/bg-11-5199-2014.

Maestrini, B., Nannipieri, P., and Abiven, S. (2014b). A meta-analysis on pyrogenic organic matter induced priming effect. *GCB Bioenergy* 7, 577–590. doi:10.1111/gcbb.12194.

Major, J., Lehmann, J., Rondon, M., and Goodale, C. (2010). Fate of soil-applied black carbon: Downward migration, leaching and soil respiration. *Glob. Chang. Biol.* 16, 1366–1379. doi:10.1111/j.1365-2486.2009.02044.x.

Masiello, C. A. (2004). New directions in black carbon organic geochemistry. *Mar. Chem.* 92, 201–213. doi:10.1016/j.marchem.2004.06.043.

Masiello, C. A., Chen, Y., Gao, X., Liu, S., Cheng, H. Y., Bennett, M. R., et al. (2013). Biochar and microbial signaling: Production conditions determine effects on microbial communication. *Environ. Sci. Technol.* 47, 11496–11503. doi:10.1021/es401458s.

Masiello, C. A., and Druffel, E. R. M. (1998). Black Carbon in Deep-Sea Sediments. *Science* 280, 1911–1914. doi:10.1126/science.280.5371.1911.

Merckx, R., den Hartog, A., and van Veen, J. A. (1985). Turnover of root-derived material and related microbial biomass formation in soils of different texture. *Soil Biol. Biochem.* 17, 565–569. doi:10.1016/0038-0717(85)90026-4.

Meredith, W., Ascough, P. L., Bird, M. I., Large, D. J., Snape, C. E., Sun, Y., et al. (2012). Assessment of hydropyrolysis as a method for the quantification of black carbon using standard reference materials. *Geochim. Cosmochim. Acta* 97, 131–147. doi:10.1016/j.gca.2012.08.037.

Moyano, F. E., Vasilyeva, N., Bouckaert, L., Cook, F., Craine, J., Curiel Yuste, J., et al. (2012). The moisture response of soil heterotrophic respiration: Interaction with soil properties. *Biogeosciences* 9, 1173–1182. doi:10.5194/bg-9-1173-2012.

Nelson, P. N., and Baldock, J. A. (2005). Estimating the molecular composition of a diverse range of natural organic materials from solid-state 13C NMR and elemental analyses. *Biogeochemistry* 72, 1–34. doi:10.1007/s10533-004-0076-3.

New, M., Lister, D., Hulme, M., and Makin, I. (2002). A high-resolution data set of surface climate over global land areas. *Clim. Res.* 21, 1–25.

Nocentini, C., Certini, G., Knicker, H., Francioso, O., and Rumpel, C. (2010). Nature and reactivity of charcoal produced and added to soil during wildfire are particle-size dependent. *Org. Geochem.* 41, 682–689. doi:10.1016/j.orggeochem.2010.03.010.

Ohlson, M., Dahlberg, B., Økland, T., Brown, K. J., and Halvorsen, R. (2009). The charcoal carbon pool in boreal forest soils. *Nat. Geosci.* 2, 692–695. doi:10.1038/ngeo617.

Openshaw, S. (1983). *The modifiable area unit problem*. Norwich (Norfolk): Geo Books.

Peters, W. J., and Neuenschwander, L. F. (1988). *Slash and burn. Farming in the Third World forest.* Moscow, Idaho: University of Idaho Press.

Preston, C. M., and Schmidt, M. W. I. (2006). Black (pyrogenic) carbon : a synthesis of current knowledge and uncertainties with special consideration of boreal regions. *Biogeosciences* 3, 397–420.

Raymond, P. A., and Bauer, J. E. (2001). Riverine export of aged terrestrial organic matter to the North Atlantic Ocean. *Nature* 409, 497–500. doi:10.1038/35054034.

Rumpel, C., Chaplot, V., Planchon, O., Bernadou, J., Valentin, C., and Mariotti, A. (2006). Preferential erosion of black carbon on steep slopes with slash and burn agriculture. *Catena* 65, 30–40. doi:10.1016/j.catena.2005.09.005.

Saiz, G., Goodrick, I., Wurster, C. M., Zimmermann, M., Nelson, P. N., and Bird, M. I. (2014). Charcoal re-combustion efficiency in tropical savannas. *Geoderma* 219–220, 40–45. doi:10.1016/j.geoderma.2013.12.019.

Santín, C., Doerr, S. H., Kane, E. S., Masiello, C. A., Ohlson, M., de la Rosa, J. M., et al. (2016). Towards a global assessment of pyrogenic carbon from vegetation fires. *Glob. Chang. Biol.* 22, 76–91. doi:10.1111/gcb.12985.

Santín, C., Doerr, S. H., Preston, C. M., and González-Rodríguez, G. (2015). Pyrogenic organic matter production from wildfires: a missing sink in the global carbon cycle. *Glob. Chang. Biol.* 21, 1621–1633. doi:10.1111/gcb.12800.

Santos, F., Torn, M. S., and Bird, J. A. (2012). Biological degradation of pyrogenic organic matter in temperate forest soils. *Soil Biol. Biochem.* 51, 115–124. doi:10.1016/j.soilbio.2012.04.005.

Schmidt, M. W. I., Noack, A. G., and Osmond, G. (2000). Black carbon in soils and sediments: Analysis , distribution , implications , and current challenges. *Global Biogeochem. Cycles* 14, 777–793.

Schmidt, M. W. I., Skjemstad, J. O., Czimczik, C. I., Glaser, B., Prentice, K. M., Gelinas, Y., et al. (2001). Comparative analysis of black carbon in soils. *Global Biogeochem. Cycles* 15, 163–167. doi:10.1029/2000GB001284.

Schmidt, M. W. I., Skjemstad, J. O., Gehrt, E., and Ko, I. (1999). Charred organic carbon in German chernozemic soils. *Eur. J. Soil Sci.* 50, 351–365.

Schmidt, M. W. I., Torn, M. S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I. A., et al. (2011). Persistence of soil organic matter as an ecosystem property. *Nature* 478, 49–56. doi:10.1038/nature10386.

Schneider, M. P. W., Hilf, M., Vogt, U. F., and Schmidt, M. W. I. (2010). The benzene polycarboxylic acid (BPCA) pattern of wood pyrolyzed between 200°C and 1000°C. *Org. Geochem.* 41, 1082–1088. doi:10.1016/j.orggeochem.2010.07.001.

Schneider, M. P. W., Smittenberg, R. H., Dittmar, T., and Schmidt, M. W. I. (2011). Comparison of gas with liquid chromatography for the determination of benzenepolycarboxylic acids as molecular tracers of black carbon. *Org. Geochem.* 42, 275–282. doi:10.1016/j.orggeochem.2011.01.003.

Shakesby, R. A., and Doerr, S. H. (2006). Wildfire as a hydrological and geomorphological agent. *Earth-Science Rev.* 74, 269–307. doi:10.1016/j.earscirev.2005.10.006.

Singh, N., Abiven, S., Maestrini, B., Bird, J. a., Torn, M. S., and Schmidt, M. W. I. (2014). Transformation and stabilization of pyrogenic organic matter in a temperate forest field experiment. *Glob. Chang. Biol.* 20, 1629–1642. doi:10.1111/gcb.12459.

Singh, N., Abiven, S., Torn, M. S., and Schmidt, M. W. I. (2012). Fire-derived organic carbon in soil turns over on a centennial scale. *Biogeosciences* 9, 2847–2857. doi:10.5194/bg-9-2847-2012.

Six, J., Conant, R. T., Paul, E. A., and Paustian, K. (2002). Stabilization mechanisms of soil organic matter: Implications for C-saturation of soils. *Plant Soil* 241, 155–176. doi:10.1023/A:1016125726789.

Skjemstad, J. O., Clarke, P., Taylor, J. A., Oades, J. M., and McClure, S. G. (1996). The chemistry and nature of protected carbon in soil. *Aust. J. Soil Res.* 34, 251–271.

Spokas, K. A., Novak, J. M., Masiello, C. A., Johnson, M. G., Colosky, E. C., Ippolito, J. A., et al. (2014). Physical Disintegration of Biochar: An Overlooked Process. *Environ. Sci. Technol. Lett.* 1, 326–332.

Thevenot, M., Dignac, M. F., and Rumpel, C. (2010). Fate of lignins in soils: A review. *Soil Biol. Biochem.* 42, 1200–1211. doi:10.1016/j.soilbio.2010.03.017.

Tinker, D. B., and Knight, D. H. (2000). Coarse woody debris following fire and logging in Wyoming lodgepole pine forests. *Ecosystems* 3, 472–483. doi:10.1007/s100210000041.

Torn, M. S., Trumbore, S. E., Chadwick, O. A., Vitousek, P. M., and Hendricks, D. M. (1997). Mineral control of soil organic carbon storage and turnover. *Nature* 389, 170–173. doi:Doi 10.1038/38260.

Vasilyeva, N. A., Abiven, S., Milanovskiy, E. Y., Hilf, M., Rizhkov, O. V., and Schmidt, M. W. I. (2011). Pyrogenic carbon quantity and quality unchanged after 55 years of organic matter depletion in a Chernozem. *Soil Biol. Biochem.* 43, 1985–1988. doi:10.1016/j.soilbio.2011.05.015.

Wardle, D. A., Nilsson, M.-C., and Zackrisson, O. (2008). Fire-Derived Charcoal Causes Loss of Forest Humus. *Science (80-.).* 320, 629. doi:10.1126/science.1160750.

Wiedemeier, D. B., Abiven, S., Hockaday, W. C., Keiluweit, M., Kleber, M., Masiello, C. a., et al. (2015). Aromaticity and degree of aromatic condensation of char. *Org. Geochem.* 78, 135–143. doi:10.1016/j.orggeochem.2014.10.002.

Wiedemeier, D. B., Hilf, M. D., Smittenberg, R. H., Haberle, S. G., and Schmidt, M. W. I. (2013). Improved assessment of pyrogenic carbon quantity and quality in environmental samples by high-performance liquid chromatography. *J. Chromatogr. A* 1304, 246–50.

Wiedemeier, D. B., Lang, S. Q., Gierga, M., Abiven, S., Bernasconi, S. M., Früh-Green, G. L., et al. (2016). Characterization, Quantification and Compound-specific Isotopic Analysis of Pyrogenic Carbon Using Benzene Polycarboxylic Acids (BPCA). *J. Vis. Exp*. doi:10.3791/53922.

Wiedner, K., and Glaser, B. (2015). “Traditional use of biochar,” in *Biochar for Environmental Management - Science and Technology*, eds. J. Lehmann and S. Joseph (London: Routledge), 15–37.

Wood, D. J. (1988). Mikrochimica Acta Characterisation of Charcoals by DRIFT. *Mikrochim. Acta* 2, 167–169.

Woolf, D., and Lehmann, J. (2012). Modelling the long-term response to positive and negative priming of soil organic carbon by black carbon. *Biogeochemistry* 111, 83–95. doi:10.1007/s10533-012-9764-6.

Zimmerman, A. R., Hall, W., and Box, P. O. (2010). Abiotic and Microbial Oxidation

of Laboratory-Produced Black Carbon (Biochar). *Environ. Sci. Technol.* 44, 1295–1301.

Zimmermann, M., Bird, M. I., Wurster, C., Saiz, G., Goodrick, I., Barta, J., et al. (2012). Rapid degradation of pyrogenic carbon. *Glob. Chang. Biol.* 18, 3306–3316. doi:10.1111/j.1365-2486.2012.02796.x.

Part B – Manuscripts

Manuscript 1

Pyrogenic Carbon in Soils: A Literature-Based Inventory and a Global Estimation of Its Content in Soil Organic Carbon and Stocks

Reisser, Moritz, Purves, Ross S., Schmidt, Michael W.I., Abiven, Samuel*

Department of Geography, University of Zurich, Winterthurerstrasse 190, 8057, Zurich, Switzerland

*Corresponding author: samuel.abiven@geo.uzh.ch

Contributions: MR and SA conceived the paper structure. MR collected the database. MR, SA, and RP contributed to the data analysis. MR and SA wrote the manuscript and all authors contributed to the writing of the manuscript.

Published: Frontiers in Earth Science / Biogeoscience, August 2016
doi: 10.3389/feart.2016.00080

Keywords: fire derived organic matter, pyrogenic carbon, soil organic matter stabilization processes, database, global distribution, soil organic carbon, global carbon cycle

Abstract

Pyrogenic carbon (PyC) is considered one of the most stable components in soil and can represent more than 30% of total soil organic carbon (SOC). However, few estimates of global PyC stock or distribution exist and thus PyC is not included in any global carbon cycle models, despite its potential major relevance for the soil pool. To obtain a global picture, we reviewed the literature for published PyC content in SOC data. We generated the first PyC database including more than 560 measurements from 55 studies. Despite limitations due to heterogeneous distribution of the studied locations and gaps in the database, we were able to produce a worldwide PyC inventory. We found that global PyC represent on average 13.7% of the SOC and can be even up to 60%, making it one of the largest groups of identifiable compounds in soil, together with polysaccharides. We observed a consistent range of PyC content in SOC, despite the diverse methods of quantification. We tested the PyC content against different environmental explanatory variables: fire and land use (fire characteristics, land use, net primary productivity), climate (temperature, precipitation, climatic zones, altitude), and pedogenic properties (clay content, pH, SOC content). Surprisingly, soil properties explain PyC content the most. Soils with clay content higher than 50% contain significantly more PyC (>30% of the SOC) than with clay content lower than 5% (<6% of the SOC). Alkaline soils contain at least 50% more PyC than acidic soils. Furthermore, climatic conditions, represented by climatic zone or mean temperature or precipitation, correlate significantly with the PyC content. By contrast, fire characteristics could only explain PyC content, if site-specific information was available. Datasets derived from remote sensing did not explain the PyC content. To show the potential of this database, we used it in combination with other global datasets to create a global worldwide PyC content and a stock estimation, which resulted in around 200 Pg PyC for the uppermost 2 m. These modeled estimates indicated a clear mismatch between the location of the current PyC studies and the geographical zones where we expect high PyC stocks.

Introduction

Fires affect about 4.64 million km2 of biomass per year, corresponding to about 4% of the earth's vegetated surface (Randerson et al., 2012). A major part of the carbon involved in these vegetation fires is emitted as CO2 into the atmosphere, yet recent studies suggest up to 15% of fire affected biomass (Santín et al., 2015) is converted into pyrogenic organic carbon (PyC; also known as fire-derived organic matter, charcoal or black carbon, Hammes and Abiven, 2013). This PyC has particular features: high relative carbon content, high chemical aromaticity, a comparably long mean residence time in the soil ranging from decades to millennia (Singh et al., 2012) and, under certain circumstances, it may have a variety of positive effects on soil properties e.g., increasing pH, water retention capacity, or nutrient availability and the retention of pollutants (Biederman and Harpole, 2013; Crane-Droesch et al., 2013). Due to these positive effects, PyC has been intentionally produced and deployed as a soil amendment, better known as biochar.

PyC is found ubiquitously in the environment (Preston and Schmidt, 2006) and soils play a key role in the PyC cycle since PyC is first deposited at the soil surface. From there, it may either physically erode, get transported by wind or water and leave the soil system or fragment into smaller pieces (Pignatello et al., 2015) and move down the soil profile where it can age, react and alter chemically and physically before being transferred to other potential pools including rivers, oceans, or sediments (Bird et al., 2015; Santín et al., 2016).

PyC content in the SOC has been approximated to represent between 0 and 35% of the total soil organic carbon (SOC; Forbes et al., 2006), but up to now, there have been few attempts to estimate complete global PyC stocks in soil. Bird et al. (2015) calculated a pool of 54–109 Pg of PyC in soil (0–100 cm depth), based on a series of assumptions regarding the PyC content in the total SOC depending on ecosystem. Santín et al. (2016) calculated a pool of 71–212 Pg of C, based on the assumption that PyC represents 5–15% of the SOC, multiplied by global SOC stocks. In both cases, the calculated amount of PyC is very sensitive to the percentage of PyC to SOC. This proportion is however unknown, and may vary as a function of not only ecosystem type (Bird et al., 2015), but also soil properties, fire characteristics, type of biomass, or climatic conditions. To date PyC distribution across ecosystems or types of soil remains unknown and furthermore we have limited knowledge as to the main parameters controlling the content of PyC in SOC.

Nonetheless, it is possible to distinguish three main groups of parameters likely to influence the PyC content in a given soil: (i) **fire and land use**: the inputs to the soil, which may vary, based on the amount and type of burning biomass, or the frequency, return interval and intensity of fires—this might further depend on the climatic zones and available feedstock but also on the land use; (ii) **climatic**: the climatic conditions, such as average temperature and moisture, which may influence decomposition or preservation patterns of PyC; (iii) **pedogenic**: the inherent physical and chemical soil parameters, including clay content and pH, play a role on the decomposition and the stabilization processes of PyC as well as the topography, which has impact on erosion rates or accumulation of PyC.

In this study, we reviewed the literature reporting content of PyC in SOC and analyzed these values as functions of these three drivers (fire and land use, climatic, and pedogenic). Our aims were: (1) to calculate the PyC stocks in soils based on published data, (2) to investigate which of the three main drivers has the largest influence on the PyC content in SOC, and (3) to show a possible application of our database, by using it in combination with other global datasets to create a global estimation of PyC contents and stocks.

Materials and Methods

Data Collection

The database was extracted from articles selected using the keywords “black carbon,” “charcoal,” “pyrogenic organic matter,” “fire-derived carbon” associated to “soil” in Google scholar and Web of Science (last search June 2015). Since our focus was on natural fire-derived organic matter, we excluded obvious cases where PyOM was added as a soil amendment (e.g., biochar) or was found as archaeological residue (e.g., hearths). We also discarded datasets where the sampling procedure was not described, the raw data not given or PyC only qualitatively described but not quantitatively. Using these criteria, we were able to collect 569 individual values, from 55 articles.

Values of PyC were reported as PyC mass % of the total SOC. When the stocks were reported, we calculated the concentration from the SOC and bulk density data. We chose to report the PyC content in SOC instead of stocks, because only 31% of the studies we collected reported PyC stock data or the bulk density values, which would be needed for stock estimations (Table 1).

Table 1. Literature extracted database description.

Parameter	Data reported	1st quarti	Median	Mean	3rd quartile
Pyrome	92.2	-	-	-	-
Vegetation	91.7	-	-	-	-
SOC [wt%]	88.1	1.14	2.46	4.19	5.63
Precipitation [mm m^{-2} yr^{-1}]	86.6	510	843	1068	1618
Temperature [°C]	80.2	7	10	10.8	14.8
pH	52.1	4.8	5.7	5.9	6.8
BDD [g dm^{-3}]	31.1	0.67	0.94	0.96	1.25
Clay [wt%]	23.1	8	19.25	22.2	30
Fire frequency [yr^{-1}] qualitative	12.1	-	-	-	-

In addition to the PyC content, we collected information corresponding to the three main drivers (fire and land use, climatic, and pedogenic). These drivers-related data were extracted directly from the articles or, if not reported, derived from other sources. Table 2 summarizes datasets, references, and assumptions used to complete the database.

Table 2. Datasets used to fill missing values or add additional investigated variables.

Variable	Extraction Method	Data Source	Limitations	Reference	Usage (inventory = *; PyC evaluation = §)
Mean Annual Precipitation (MAP)	Join attributes by coordinates	Precipitation map	Only mean, no variability included	(New et al., 2002)	*§
Mean Annual Temperature (MAT)	Join attributes by coordinates	Temperature map	Only mean, no variability included		*§
Köppen-Geiger Zone (KG)	Join attributes by coordinates	Köppen-Geiger Map	Strongly generalized	(Kottek et al., 2006)	*
Altitude	World Elevation Service of ESRI	USGS GTOPO 30 and SRTM 90m	No information on relief and interpolated	(ESRI, 2016)	*
Clay Content	Join attributes by coordinates	HWSD	Interpolated and modelled data	(FAO/IIASA/ISRIC/ISSCAS/JRC, 2012)	§
pH	Join attributes by coordinates	HWSD	Interpolated and modelled data		§
Soil Organic Carbon content (SOC)	Join attributes by coordinates	HWSD	Interpolated and modelled data		§
Bulk Dry Density (BDD)	Join attributes by coordinates	HWSD	Interpolated and modelled data		§
Pyrome	Join attributes by coordinates	Pyrome dataset	Only a concept	(Archibald et al., 2013)	*§
Fire Frequency	Join attributes by coordinates	Pyrome dataset	Data since two decades		*
Fire Intensity	Join attributes by coordinates	Pyrome dataset	Data since two decades; resolution of acquisition and fires do not match at all.		*
Net primary Productivity	Join attributes by coordinates	NASA npp dataset	Modelled data, derived from proxies	(Zhao et al., 2005)	*
Land Use	Join attributes by coordinates	NASA land cover dataset	Derived from proxies	(Friedl et al., 2010)	*§

We included the altitude using the World Elevation Service of ESRI© (ESRI, 2016), which is derived from the GMTED2010 data set (Danielson and Gesch, 2011). Remote sensing data were used to associate Köppen-Geiger climate zone (KG; Rubel and Kottek, 2010), net primary productivity (from the NASA NPP dataset) and the fire regime, based on the concept of pyromes, as proposed by Archibald et al. (2013), including also the raw fire return interval (FRI) and fire-frequency data to our dataset. According to this pyrome concept, the terrestrial ecosystems are divided into five different zones characterized by fire intensity and return interval: frequent intense large (FIL), frequent cool small (FCS), rare intense large (RIL), rare cool small (RCS), and intermediate cool small (ICS). Frequent occurrence corresponds to annual fires, while rare occurrence corresponds to a return period of more than 50 years. The intensity is based on the fire radiative power. Small fires correspond to areas smaller than 25 km2, while large fires correspond to areas larger than 100 km2. When existing in the article, we also added the on-site fire frequency, but fire history was not consistently reported in the literature. In some cases, only qualitative information was given (e.g., “high” or “low”). All data were transformed to these nominal categories as follow: less than every 10 years = high; 10–100 years = medium; less fires than every 1000 years = low.

We also included the land use (forest, grassland, agriculture, peatland, urban, shrubland) from the NASA MODIS land cover product, the mean annual precipitation (MAP) and mean annual air temperature (MAT), soil type, bulk density, sampling depth, SOC the clay content, and soil pH. All these parameters were extracted directly from the articles, or from reference datasets (Table 2).

Soil depth was distinguished into top- and subsoil, where topsoil was defined as the uppermost 10 cm and subsoil as soil horizon below this limit. There was no significant difference (95% confidence interval) between these two soil depths so the data set was analyzed considering the whole soil profile. In order to compare continuous and discrete variables, parameters were categorized into 5–7 groups according their initial distribution.

Representativeness of the Dataset

The percentage of data available in the database as well as the median, average and the quartile values for continuous data are given for each parameter in Table 1. The vegetation related parameters are well represented in the database, while soil parameters were present in <50% of the studies. Local fire history was indicated in

only 12% of studies. Interpretation of patterns can be strongly limited, depending on this availability of local data.

The distribution of each parameter in the dataset was compared to its worldwide distribution extracted from a reference database [i.e., soil parameters like pH, clay content, and SOC content from the harmonized world soil database (FAO/IIASA/ISRIC/ISSCAS/JRC, 2012) and the pyromes from Archibald et al. (2013)]. The distribution histograms are present in Figures 5, 6.

Quantification of PyC

A wide variety of methods exist to quantify the PyC in soil. It has been shown in the past that these methods do not always yield the same results for a given sample (Schmidt et al., 2001; Hammes et al., 2007). In this work, we considered six major different methods:

(i) Physical method: simple visual assessment (charcoal pieces counting), generally done with the naked eye or under microscope und mostly preceded by a physical separation step (for example flotation);

(ii) Chemo-thermal oxidation method (CTO 375; Gustafsson et al., 1997, 2001): the soil sample is exposed to strong oxidants, mainly trifluoroacetic acid and HCl and heated up to 375°C in an oven. This method includes a decarbonization step, which can be conducted after (Gustafsson et al., 1997) or before (Gustafsson et al., 2001; Bucheli et al., 2004) the thermal treatment. Both versions of the methods were accepted in this work. Quantification of the PyC residual is usually done by elemental analysis.

(iii) Dichromate oxidation method: the soil is treated with K2Cr207, a very strong oxidant, which is supposed to oxidize all labile organic carbon and the residual is considered oxidation resistant elemental carbon (OREC; Bird et al., 1999). These OREC values are also quantified with an elemental analyser and are multiplied by 2.36, using the factor proposed by Knicker et al. (2008);

(iv) Benzenepolycarboxylic acid (BPCA) molecular marker method, initially developed by Glaser et al. (1998). In this method, PyC is broken down with help of HNO3 into specific BPCAs, which can be quantified with either gas or liquid chromatography (Schneider et al., 2011; Wiedemeier et al., 2013) using a standard. The conversion factor of 2.27 (Glaser et al., 1998) was used to calculate the actual PyC;

(v) UV oxidation: PyC is considered as the organic residues after a strong UV irradiation treatment. Quantification is achieved by comparison of the material before

and after treatment, using solid-state 13C nuclear magnetic resonance (NMR) spectroscopy (Skjemstad et al., 1996).

(vi) NMR method: the PyC content in SOC is estimated directly from the NMR spectrum, using a mixing model (Nelson and Baldock, 2005), without any chemical or physical separation step.

Any other reported methods were grouped under the label “others.”

Statistical Analysis

All continuous variables, except MAP and MAT, were grouped into five to seven groups, in order to allow the comparison of the database with to global distributions. Grouping was done according to relevant physical thresholds for each parameter and aiming for a balanced grouping, i.e., roughly the same number of points in each group. Data were log transformed to conform them to normality. These variables were tested with a One-Way ANOVA using R statistics (R Core Team, 2015) against the PyC concentration as a percentage of SOC. We conducted Student-Newman-Keuls *post-hoc* tests in order to compare groups with each other (difference tested for $p < 0.05$). MAT and MAP were tested with Spearman's rank correlation ρ.

Case Study: Global Evaluation of the PyC Content and Stocks

In order to show the potential of our database, we created a linear model in combination with other existing global datasets for a global evaluation of PyC content in SOC and stocks. First, we filled the missing values in the dataset with values from the global datasets by joining the attributes in QGIS© (QGIS Development Team, 2015): clay, pH, and SOC with the harmonized world soil database (FAO/IIASA/ISRIC/ISSCAS/JRC, 2012), a temperature and precipitation dataset (New et al., 2002), the land cover dataset from NASA (Friedl et al., 2010), and the fire-frequency dataset of Archibald et al. (2013). Dataset description and related assumptions are compiled in Table 2.

A linear model was then fitted on this extended database using R. After simplification, the model corresponded to the Equation (1):

$$\log(\mathrm{PyC}) = \mathrm{clay} + \mathrm{pH} + \mathrm{MAP} + \mathrm{MAT} + \text{land use} + \varepsilon \quad (1)$$

Where PyC is the PyC content as % of SOC,clay the % of clay in soils, pH the pH of the soil, MAP the mean annual precipitation from the database, extracted as described above, MAT the mean annual temperature from the database, extracted as

described above, land use the different categories of land use in the database and ε the error term, which accounts for the variability which can't be explained by the considered variables.

Together, the variables explained 33% of the total variance in the dataset (more detailed statistics are shown in Table 3). We then applied this model to predict the PyC content in SOC at a resolution of 20 km to produce a global map. PyC stocks were calculated by multiplying the values with the bulk dry density (BDD) and SOC content. As the maximum depth of the used soil parameters was 200 cm, the model does not predict anything deeper than these 200 cm.

Table 3. Summary of the model statistics used for the global evaluation.

Residuals:

Min	1st Quartile	Median	3rd Quartile	Max
-4.8932	-0.4427	0.0455	0.5346	2.4265

Coefficients:

	Estimate	Std. Error	t value	Pr(>|t|)	Lvl of signif.
(Intercept)	2.34	0.56	4.17	3.70E-05	***
clay 0-5%	-1.00	0.42	-2.40	0.017	*
clay 5-10%	-1.04	0.39	-2.71	0.007	**
clay 10-25%	-0.87	0.36	-2.41	0.016	*
clay 25-50%	-0.61	0.36	-1.67	0.095	.
pH 4-5%	0.16	0.28	0.57	0.568	
pH 5-6%	0.48	0.26	1.84	0.067	.
pH 6-7%	0.45	0.28	1.59	0.113	
pH >7%	0.77	0.28	2.80	0.005	**
MAP 0-600	-0.38	0.19	-1.96	0.051	.
MAP 601-1200	-0.55	0.18	-3.09	0.002	**
MAP 1201-1800	-0.76	0.19	-3.90	0.000	***
MAP 1801-2400	0.44	0.21	2.06	0.040	*
MAT 0-7.5°	0.89	0.25	3.51	0.000	***
MAT 15-22.5°	0.77	0.28	2.75	0.006	**

MAT 7.5-15°	0.91	0.24	3.74	0.000	***
MAT >22.5°	0.87	0.30	2.94	0.003	**
Forest	-0.40	0.14	-2.95	0.003	**
Grass	-0.28	0.10	-2.65	0.008	**
Peat	0.07	0.33	0.22	0.825	
Shrub land	-0.77	0.23	-3.26	0.001	**
Urban	-1.00	0.22	-4.60	5.47E-06	***

Signif. codes: 0 < '***' < 0.001 < '**' < 0.01 < '*' < 0.05 < '.' < 0.1 < ' ' < 1

Residual standard error: 0.844 on 467 degrees of freedom

Multiple R-squared: 0.3587 Adjusted R-squared: 0.3298

F-statistic: 12.44 on 21 and 467 DF

p-value: < 2.2e-16

Results

PyC Content in the SOC

Figure 1 presents the PyC content distribution histogram from our literature database. Values range between 0 and 50% with one outlier above 60% (Caria et al., 2011): first quartile at 5.2%, median 12.3%, third quartile 18.6%, and the arithmetic mean at 13.7%.

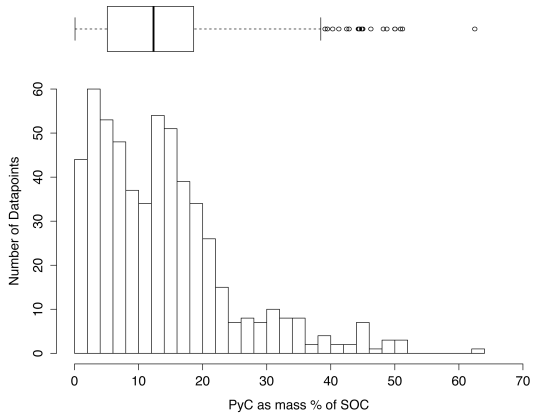


Figure 1. Frequency histogram of PyC content as mass % of the total SOC for the entire database (n = 569). Each column represents an increment of 2% of the PyC content.

Method Comparison and Data Representativeness

As described above, the diversity of quantification methods existing in the literature may induce bias in the collected data on PyC content in SOC. Figure 2 presents the PyC values according to the analytical method used to determine the PyC content in the soil samples. The K2Cr2O7 oxidation, the NMR, and the UV oxidation methods present significantly higher values (16.9, 17.6, and 17.6% in average, respectively; $p < 0.001$) than the BPCA (11.3%), CTO 375 (12.5%), and the physical approaches (10.1%). These differences are in line with the literature focussing on method comparisons (Hammes et al., 2007; Bird, 2014), with however, much smaller variations in than in these systematic comparison. In these previous studies, content of PyC in SOC varied by several factors of magnitude depending on the type of sample analyzed. Here the differences, observed for different samples, are on average only of few per cent. For all the methods except NMR, the range of PyC measured is large, from about 0 to more than 30% in all cases, meaning that all the methods are able to detect very low and very high levels of PyC. So, despite small variations, we consider that the choice of the quantifying method does not play a major role in the database analysis.

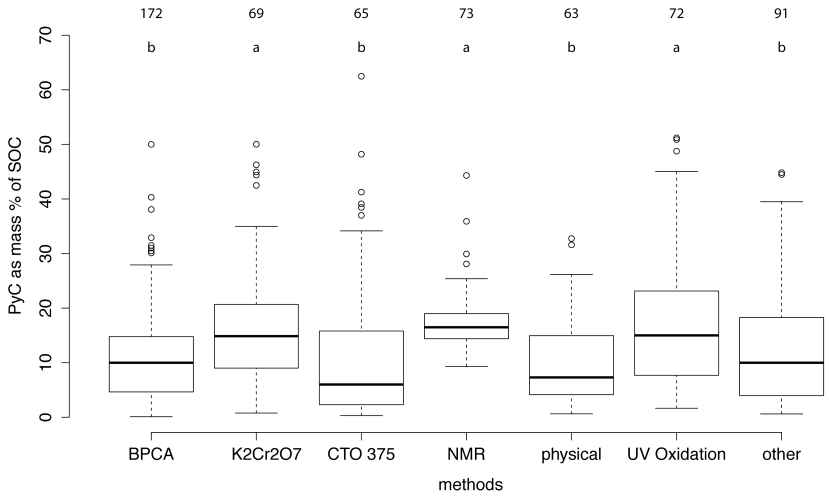


Figure 2. PyC content as mass % of the total SOC as a function of the methods used in the literature database and their respective PyC content distribution as mass % of total SOC. One-Way-ANOVA for the methods results in a $p < 0.001$. The different letters on the top indicate significant differences ($p < 0.05$ TukeyHSD test) between the methods.

Another issue concerns the spatial representativity of the database. Figure 3 presents the world wide geographical distribution of the sites from which the literature data were collected. Africa, central Russia, high latitudes, and southwest Asia are almost absent of the database, while Europe and North America are heavily

represented. The PyC content does not seem to be related to large-scale spatial patterns: for example within Europe a very large range of PyC values can be observed (data not shown). This heterogeneity is a clear weakness of this database and more generally of the literature related to PyC in soils.

Figure 3. Spatial distribution of the PyC values which were published and taken into account in our database.

PyC Content in the SOC As a Function of Fire Characteristics

Figure 4 presents the content of PyC in SOC as a function of the fire intensity and -frequency, defined by the pyrome concept (a), the global FRI dataset (b), or the local fire frequency, for a subset of samples where this information was available (n = 64, less than 12% of the whole dataset) (c).

Surprisingly, almost no difference was observed between pyromes. Despite clear fire characteristic differences in terms of fire return period and intensity, the resulting PyC contents in SOC were very similar between the different pyromes. The only difference was observed for the zone with frequent, large and intense fires (FIL), where lower PyC contents were observed (4.8%).

The PyC content in SOC is also not related to the global FRI. Values range from 12.1% in regions with very long FRIs to 14.3% in regions with very frequent fires. This may be due to the resolution (1 km) of the FRI dataset, which may not capture local fire properties.

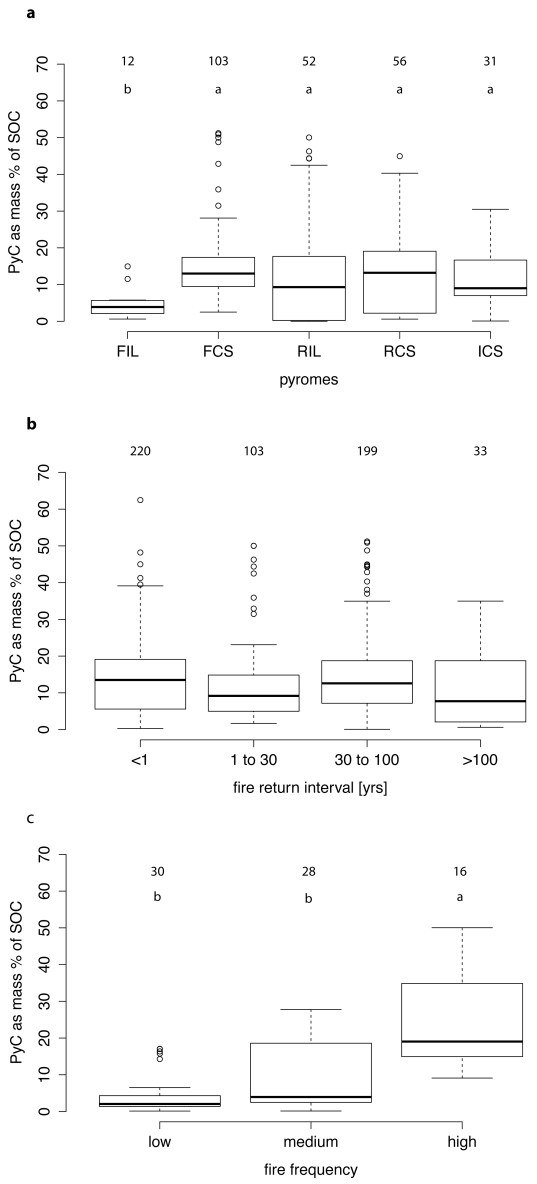


Figure 4. PyC content as mass % of the total SOC described by fire parameters: the pyromes of Archibald et al. (2013) (A); global fire return interval (B); on-site fire-frequency information (C). One-Way-ANOVA results in $p < 0.001$, < 0.001, and 0.19 for the pyromes, the global fire return interval, and on-site fire frequency, respectively. The different letters on the top indicate significant differences ($p < 0.05$) within the datasets.

When the site has a clear reported fire history, the fire frequency has a significant effect ($p < 0.001\%$) on the PyC content (Figure 4C). Sites with high frequency contain about twice the PyC, 24.4%, compared to values of 9.2 and 4.5% respectively for medium and low fire frequencies.

PyC Content in the SOC As a Function of Land Use

The highest content of PyC in SOC was found in soils used for agriculture (16.0%; Figure 5). The corresponding samples were not only collected on sites where traditional slash and burn-like techniques are still in use, but also in Europe and North America, where this specific technique has not been widely used as an agricultural practice for at least a century (Peters and Neuenschwander, 1988; Wiedner and Glaser, 2015).

The PyC content is lower in grasslands and forests than in agricultural land, with forests presenting the lowest content of PyC in SOC of all the land use types (9.7%). Grassland PyC content was slightly higher with a mean of 12.1%. Peatland and urban land uses had values of 12.3 and 10.8% respectively.

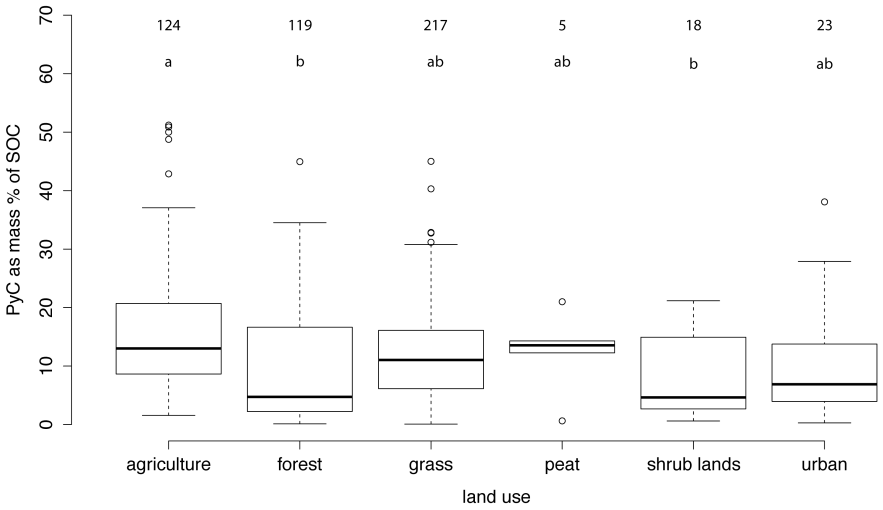


Figure 5. PyC content in % as mass of the total SOC described by different land use types. One-Way-ANOVA results in $p < 0.001$. The different letters on the top indicate the significant differences ($p < 0.05$) between the different land uses.

PyC Content in the SOC As a Function of the Climatic Conditions

Content of PyC in SOC does not follow a consistent trend when compared to the annual precipitation (Figure 6A). Dry and wet sites show similar PyC content in the SOC. Spearman's correlation coefficient was very low ($\rho = -0.02$). We observe a clearer trend for mean annual temperatures (Figure 6B). Colder sites (especially below 0°C) present lower PyC content than warmer sites with a maximum around 10°C, even slightly decreasing toward warmer temperatures. Here, a clear correlation could be found ($\rho = 0.33$; $p < 0.0001$). This positive temperature effect can be related to different factors: biomass productivity promoted by higher temperature, higher probability of fires starting under warmer conditions or/and higher decomposition rate of PyC in the soil in warmer climate zones, compared to colder zones.

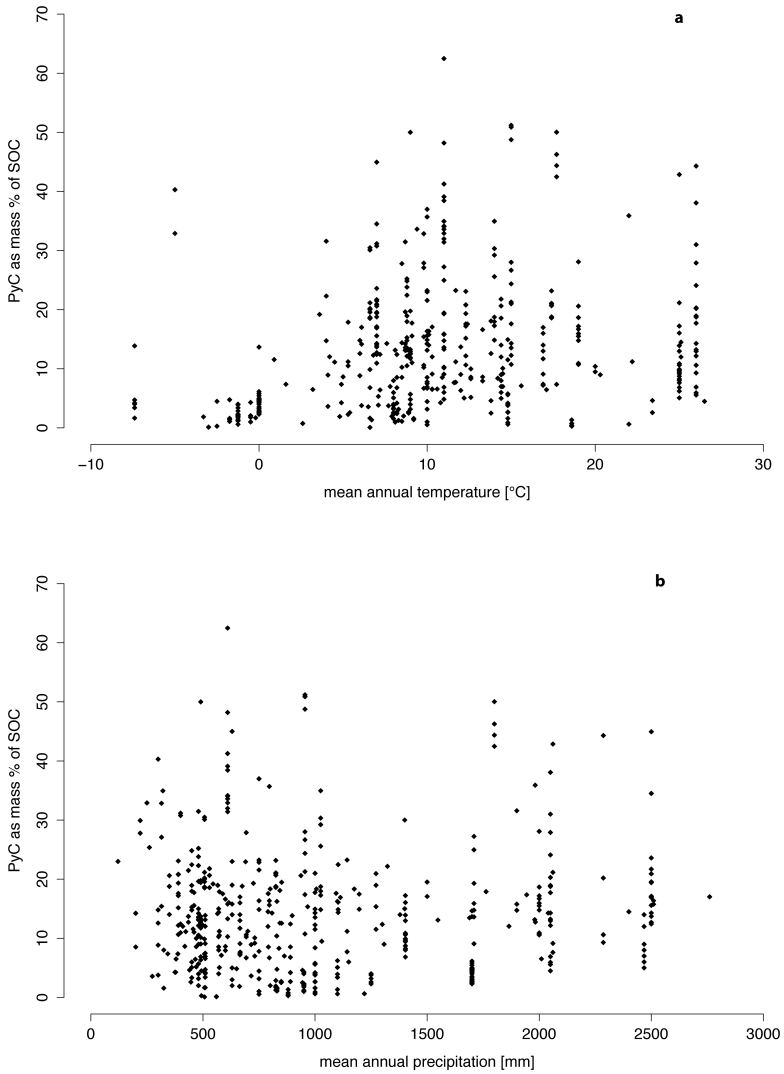


Figure 6. PyC content as mass % of the total SOC plotted against climatic variables: mean annual precipitation (A) and mean annual temperature (B). Spearman's rank correlation yielded a *p*-value of 0.66 and a rho of −0.02 for the precipitation and a $p < 0.001$ with a rho of 0.33 for the temperature.

Figure 7 shows the content of PyC in SOC as a function of the KG climate zone. The highest PyC content is found in the equatorial (16.8%) temperate (15.5%) and desertic zones (12.7%). These three systems are significantly richer in PyC ($p <$ 0.001%) than the continental (8.9%) and the polar zones (4.4%), respectively and mirror the trends observed in the temperature data, above all for the polar sites, where low PyC content coincides with very little fire, slow decomposition and possible break down, due to freeze-thawing. The database has generally a

representative distribution in the KG zones, except for the temperate zone (over-represented) and the polar zone (under-represented).

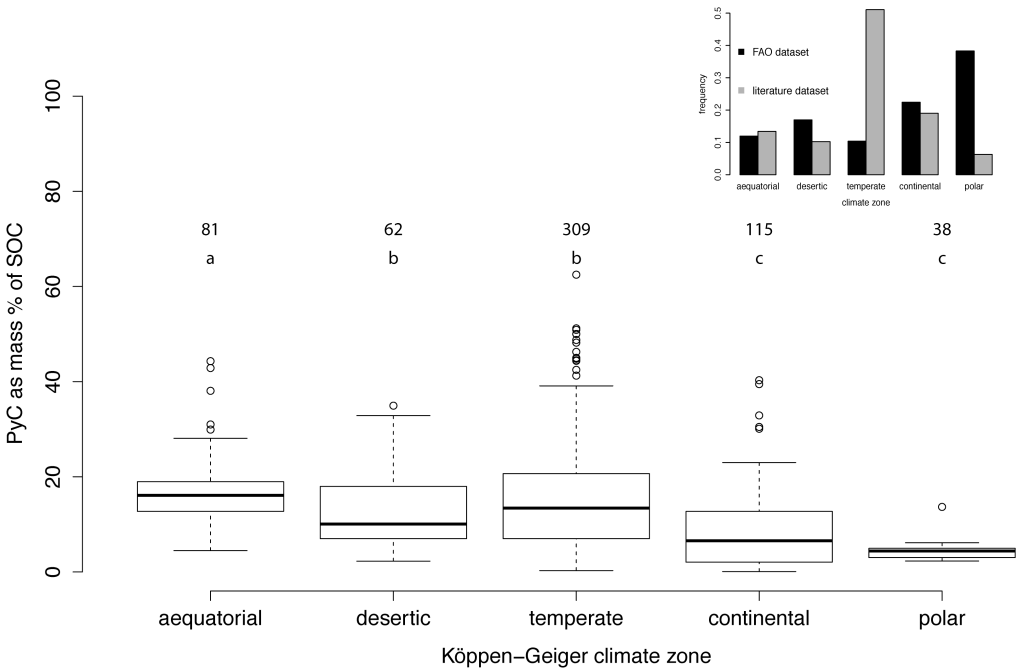


Figure 7. PyC content as mass % of the total SOC as a function of the climatic zone. Only the five KG supergroups were used. Equatorial relates to all groups starting with a A in the KG classification, desertic with a B, temperate with a C, continental with a D and polar with a E. The One-Way-ANOVA resulted in a $p < 0.001$. The different letters on the top indicate the significant differences ($p < 0.05$) between the different KG zones.

PyC Content in the SOC As a Function of the Soil Characteristics

The content of PyC in SOC seems to be more directly related to the soil properties. First, PyC content in the SOC is significantly related ($p < 0.001\%$) to the clay content (Figure 8a). When the clay content is higher than 50%, the PyC content was on average more than twice that of lower clay contents (32.7% compared to 12–14%). When the clay content of the soil was between 0 and 5%, then the PyC content was much lower (5.7%). Our database represents relatively well the clay content distribution worldwide (as described by the harmonized world soil database), with the notable exception of an underrepresentation of low clay content soils.

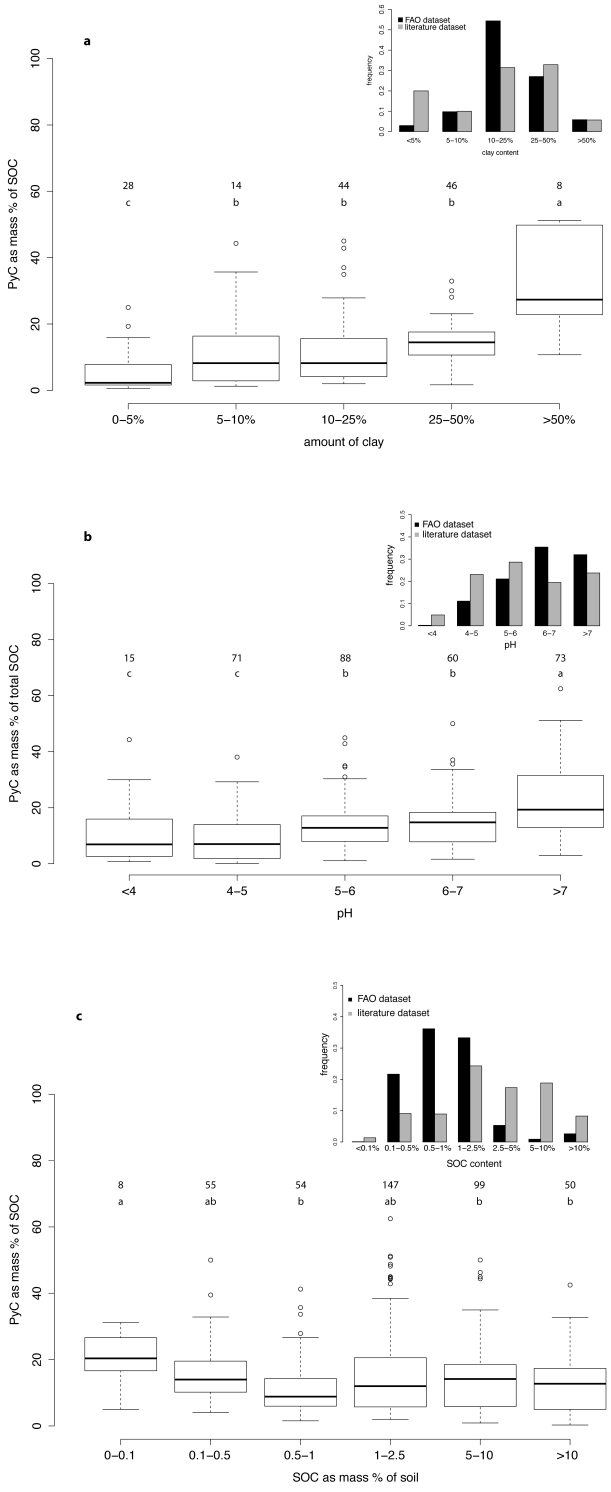


Figure 8. PyC content as mass % of the total SOC described by different soil parameters: The clay content (A); pH (B); total SOC content (C). The One-Way-ANOVA resulted in $p < 0.001$ for the clay content, <0.001 for the pH, and <0.01 for the SOC content. The different letters on the top indicate the significant differences ($p < 0.05$) within each dataset.

Soil pH also has a statistically significant ($p < 0.001\%$) and large effect on the PyC content in SOC (Figure 8b): a pH above 7 translates into larger PyC content than between 6 and 7 (21 vs. 14.9%), and acid soils (below 5) contained much less PyC (8.6–11.7%).

The overall SOC content seems to have also an influence on its relative PyC proportion (Figure 8C). Soils with low SOC content (0–0.1% and to a lesser extent 0.1–0.5%) have a significantly ($p < 0.01\%$) higher PyC content in its SOC than SOC-rich soils. However, the distribution of our database favors high SOC content and the number of samples with low SOC content is relatively low compared to the global distribution.

Discussion

PyC Content in the SOC

Our large collection of data is globally in line with previous estimations of the content of PyC in the SOC. We observed a mean of 13.7% of the SOC, ranging from 0 to 60%, while previous estimations ranged from 0 to 35% (Forbes et al., 2006; Bird et al., 2015; Santín et al., 2016).

Compared to other specific identified compounds in soils, PyC seems to be a major contributor to the SOC: lignin content ranges only between 0 and 6%, with an average around 1.5% of the SOC (review of 27 studies by Thevenot et al., 2010); soil lipids rarely exceed 2% of the SOC (Dinel et al., 1990); carbohydrates have a comparable distribution (5–20%; Lowe, 1978), however very few recent estimates exist for the latter two groups of compounds.

In comparison to the above mentioned compounds, fire-derived organic matter enters the soil usually only sporadically and in relative small quantities (the biomass transformation rate to PyC is estimated to be around 1–26% during a fire; Czimczik et al., 2003; Forbes et al., 2006; Eckmeier et al., 2007; Santín et al., 2015), compared to lignin which represents a continuous or seasonal input of >20% of the litter (Thevenot et al., 2010) to the SOC.

Drivers Explaining PyC Content in the SOC

Our analysis of the content of PyC in SOC drivers leads to an unexpected new picture on PyC distribution in soils. Fire characteristics as reported here do not seem to play a major role in the constitution of a PyC stock. Neither pyromes nor the FRI can explain the PyC content patterns. The only significant factor corresponds to very intense fires at a local scale, indicating, that fire impacts can be seen only very locally. Land use also gives an interesting picture: higher contents of PyC in the SOC in agricultural soils than in grassland and forests, respectively. On the other hand, the PyC content variations correlated very well with soil properties, i.e., higher clay and pH lead to high PyC%.

Soil properties clearly define conditions for stabilization of PyC. Higher clay content might lead to more organo-mineral interactions (Sørensen, 1972; Merckx et al., 1985; Hassink, 1997; Six et al., 2002) and higher pH to less decomposition of PyC in general. Archaeologists usually use the pH as a parameter to identify sites where charcoal remains may be found (Braadbaart et al., 2009), well in accordance with our observations. Fresh organic matter decomposes slower at low (5.0) and high (8.0) pH (DeLaune et al., 1981). However, soil respiration tends to be higher at high pH

than at low pH (Kemmitt et al., 2006; Aciego Pietri and Brookes, 2008), indicating that alkaline conditions do not always imply a lower microbial activity. In a manipulative experiment, Braadbaart et al. (2009) observed an increase in the charcoal fragmentation in alkaline solutions, probably because of the cation (Ca^{2+} and K^{+}) transfer inside the graphitic structure of the charcoal pieces. These smaller particles may be easier to stabilize on the long term, since they can bind more directly to minerals in finer fractions of the soil (Nocentini et al., 2010).

However, the three types of drivers we identified earlier cannot be exactly compared. Both spatial and temporal scales are problematic for information related to land use, fire characteristics, or even climate. These parameters may vary greatly over the time, particularly at the time scale we are considering here. Several authors reviewed the literature related to PyC turnover in soil and the estimates vary between 100 and 1000 years (Preston and Schmidt, 2006; Lehmann et al., 2008; Liang et al., 2008; Singh et al., 2012). At this time scale, information on fire frequency and intensity, land use or climate may vary greatly, while PyC in the soils remains relatively unchanged over long timescales. This all indicates, that we may see a temporal mismatch between our measured PyC and its predictors with which we try to explain it. For example, the higher content of PyC in the SOC in agricultural land might not be explained by the recent land use, but could be linked to stubble burning in the last century, or even much older agricultural practices from the Middle Ages or earlier, which may have included much more common use of fire. Another explanation might be the relative preservation of PyC due to increased SOC turnover by tillage and generally agricultural practices. Yet, one might also speculate that PyC-rich soils, being more fertile, have been turned into agricultural land more often than other lands, and thus that we would observe a feedback between PyC stocks and land-use over long time scales.

Fire frequency derived from remotely sensed satellite data cannot cover more than the last two decades, due to the availability of data (Dwyer et al., 2000; Archibald et al., 2013; Bowman et al., 2014). Furthermore, the spatial resolution of the data does most often not mirror the natural heterogeneity of fires very well. Even if only parts of a pixel burn, it is stated that this specific pixel burnt. However, one might still find places in this pixel, which were not affected by fire at all.

When the history of fire is known for a given place, the fire frequency is more relevant.

Compared to fire characteristics, land use or even climate, soil properties are relatively constant and are more integrative of the time where PyC effectively spent in the soil. It may be a reason why soil parameters appear particularly relevant for the PyC content.

Case Study: Global Evaluation of the PyC Contents in the SOC and Stocks

Observations

Modeled PyC values are slightly lower than the literature dataset (Figure 1). The mean is 8.7%, the median is 7.5% with the first quartile at 5.8% and the third quartile at 10.5%. This is unexpected, since the five parameters in the model are relatively well distributed in the initial database, so we expected modeled values closer to the literature. One consequence might be that either the model underestimates the total content of PyC in the SOC or the database rather overestimates it.

Figure 9 shows the maps for the global PyC content in total SOC and Figure 10 for the stocks. Highest PyC contents are found mostly in the large steppe regions of between around 23° and 50° north, as well as in Patagonia and in tropical rainforests. These high values could be explained for a large part by the pH and clay content of the soils, two of the five parameters of the model. Lowest concentrations are above all situated in boreal regions on the northern hemisphere.

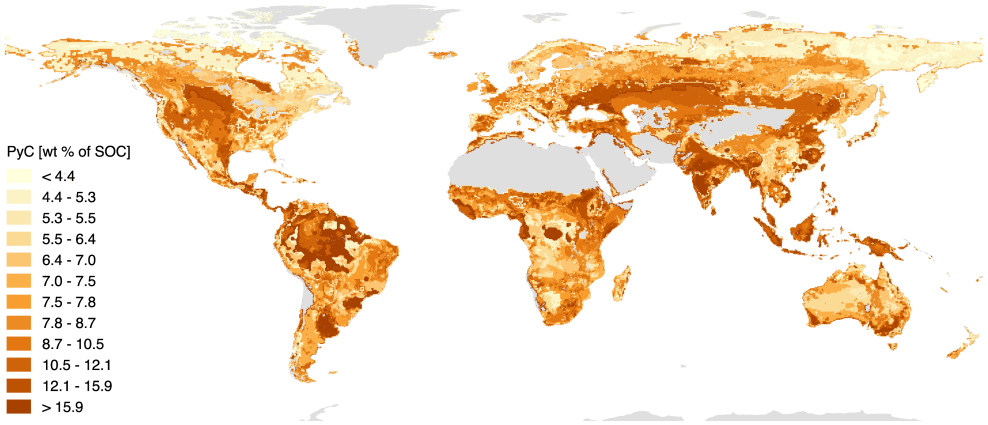


Figure 9. Global predicted PyC content as mass % of the total SOC. Explained variance by the used linear model is 33%. Variables used were clay content, pH, mean annual precipitation, mean annual temperature, and land use. Land mass is colored in gray.

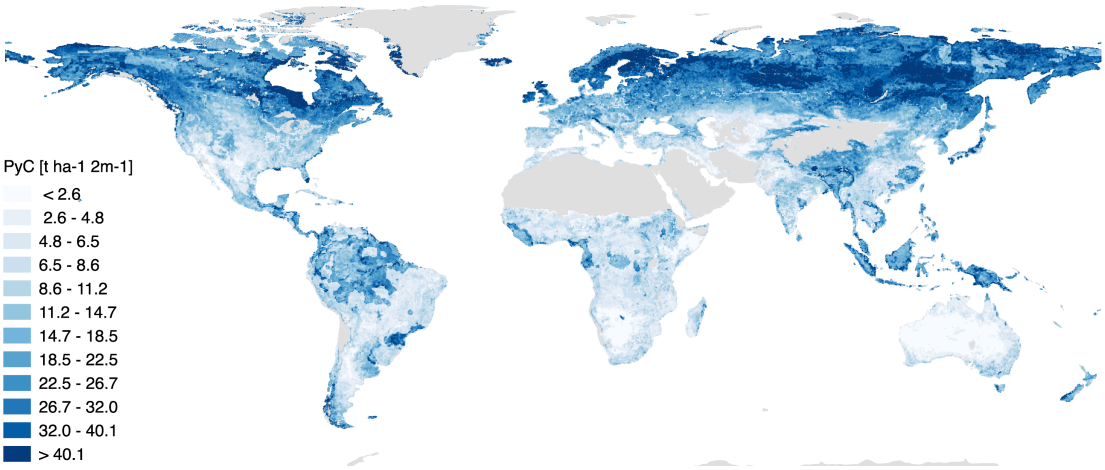


Figure 10. Global predicted PyC stocks as t ha–1 for the first 2 m soil depth. Explained variance by the used linear model is 33%. BDD and total SOC content from the global dataset were used to calculate the stocks from the PyC content in SOC data. Land mass is colored in gray.

The picture changes radically in most regions when it comes to stocks. Very high PyC stocks are found in the boreal zones. PyC contents in the SOC are low in boreal areas but SOC stocks are very important, while in some other regions PyC contents are high, for example in Australia, Africa, and the Indian sub-continent, but the SOC stocks are much lower and thus the PyC stocks are also low. In tropical regions, both the content of PyC in the SOC as well as the SOC stocks are high. Global PyC stock is estimated, based on the integration of all values to be roughly around 200 Pg.

Limitations and Perspectives

Based on a large data collection from the literature, we propose here the first global estimation of PyC content as a function of SOC in soils. Based on this estimation, we are able to identify hotspots of PyC presence. Some of these locations are not surprising, for example where chernozems or mollisols can be found. More unexpected are locations such as tropical forests, which seem to yield high contents of PyC in SOC as well. The high clay and low SOC contents would explain these patterns. It does not seem that one simple rule can explain high levels of PyC in soils, but rather a conjunction of soil properties (pH or clay, both parameters do not need to be met) and ecosystem properties (large biomass in tropical forests, frequent fires on easy fragmentable grass material in central Asia). This would also indicate that the qualitative properties related to this PyC (chemical functions, physical structure) might also vary greatly with the region. On the other hand, we can identify zones where in absolute numbers only very little PyC can be found, despite frequent

fires or apparent other favorable conditions for high PyC content. This is the case for large parts of Australia, where stocks are largely limited through the small overall SOC stocks, or boreal forests. Both regions were used frequently in previous studies. As for the hotspots, it is difficult to identify a unified explanation for these low values. There is a need to selectively identify the main missing drivers at a regional scale. The example of boreal forests is particularly interesting. This ecosystem is prone to fire, and decomposition rate should be highly reduced by low temperature and high moisture content. From this point of view, it is comparable to high latitude soils. However, the literature dataset and the global evaluation indicate rather low PyC contents in the SOC, compared to other climatic zones. This can only be explained by parameters we did not take into account in our analysis, such as lateral transport in the landscape, the combustion of the PyC by successive fires (although estimated to have only small influence; Santín et al., 2013; Saiz et al., 2014; Tinkham et al., 2016) or higher degradability of PyC which is produced at lower temperature (Schneider et al., 2010; Ascough et al., 2011; McBeath et al., 2015).

Since the variation range of SOC is much larger than the PyC one (in particular, our estimation tends to reduce this range), the largest projected PyC stocks appear in zones that are not directly related to fire or PyC stabilization parameters. The largest stocks are in high latitude soils where it is probable that little PyC content is present per unit of SOC, but where large stocks of SOC are stored. Tropical forests would be the location where both content and stocks are within the highest on the planet.

Our model has also a series of limitations. First, it explains only 33% of the total variance. This rather low power can be explained by different reasons: the time and space scale mismatch between the parameters and the PyC content dynamics (see above), the location of the sampling places or the method multiplicity. There are important differences in the location of the original sites from the literature and the global evaluation of PyC by our model. Most of our data come from Europe, East Australia and Northern America, while larger contents in the SOC are expected in boreal forest and central Asian steppes and larger stocks in high latitude soils. A direct consequence of this bias is that our evaluation rather tends to underestimate the content of PyC in SOC overall. Some zones are not explored at all, including for example most of Africa, southern Asia or central Russia, locations where high PyC contents in the SOC would be expected.

The diversity of methodological approaches may also be an issue. Hammes et al. (2007) and more recently Bird (2014) showed that a large range of PyC contents

could be measured on a given sample depending on the method used. In this study, we considered seven methods, surprisingly giving consistent and comparable results. If we consider that there is no potential systematic bias that would associate a method to samples with intrinsic lower or higher PyC samples, this relative comparability around the same average value rather contradicts the existing literature. One explanation would be that when studies compare different methods to detect PyC, they use mainly PyC rich material (chernozem, pure charcoals, soot samples, etc.) and so artificially increase the range of values detected. In our case, since all types of soils are included, the differences between the values produced are not that important anymore. As a conclusion, we expect the different methods to have only a minor impact on the complete picture.

Conclusion and Perspectives

Based on a large literature database, we assessed the content of PyC in SOC, investigated a variety of drivers related to PyC production and ecosystem properties to explain these contents. Then we used these in combination with several other datasets to model the distribution of PyC on a global scale. Our key achievements and findings are as follows:

• We have produced the first unified database of published PyC measurements;

• PyC represents on average around 14% of the SOC, corresponding to one of the largest identified groups of chemical compounds in soil;

• High soil pH and clay content are the most significant parameters explaining a high PyC content in the SOC;

• PyC production parameters, such as fire or land use, do not well explain PyC content patterns.

• There is a temporal mismatch between the time scales over which PyC is expected to vary and the time scales over which it (and its related variables) are observed.

• There is a spatial mismatch between the regions with expected high PyC stocks and those, which are actually studied.

• There are still many limitations to overcome, if we want to improve our global picture of PyC, for example data scarcity in remote locations, resolution and derivation of global datasets or quantification method comparability.

The database is available in the Supplementary Material and can be used for other studies. We want to encourage scientists to improve the database, expand it with other variables or find new ways of filling the gaps and missing values.

Author Contributions

MR and SA conceived the paper structure. MR collected the database. MR, SA, and RP contributed to the data analysis. MR and SA wrote the manuscript and all authors contributed to the writing of the manuscript.

Conflict of Interest Statement

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Acknowledgments

We thank S. Archibald for providing the fire dataset. We also thank the reviewers for their valuable comments. This research is supported by the University of Zurich, through the URPP GCB (University Research Priority Program Global Change and Biodiversity).

References

Agarwal, T., and Bucheli, T. D. (2011). Adaptation, validation and application of the chemo-thermal oxidation method to quantify black carbon in soils. *Environ. Pollut.* 159, 532–538. doi:10.1016/j.envpol.2010.10.012.

Andreeva, D. B., Leiber, K., Glaser, B., Hambach, U., Erbajeva, M., Chimitdorgieva, G. D., et al. (2011). Genesis and properties of black soils in Buryatia, southeastern Siberia, Russia. *Quat. Int.* 243, 313–326. doi:10.1016/j.quaint.2010.12.017.

Ansley, R. J., Boutton, T. W., and Skjemstad, J. O. (2006). Soil organic carbon and black carbon storage and dynamics under different fire regimes in temperate mixed-grass savanna. *Global Biogeochem. Cycles* 20, n/a–n/a. doi:10.1029/2005GB002670.

Boot, C. M., Haddix, M., Paustian, K., and Cotrufo, M. F. (2014). Distribution of black carbon in Ponderosa pine litter and soils following the High Park wildfire. *Biogeosciences Discuss.* 11, 16799–16824. doi:10.5194/bgd-11-16799-2014.

Brodowski, S., Amelung, W., Haumaier, L., and Zech, W. (2007). Black carbon contribution to stable humus in German arable soils. *Geoderma* 139, 220–228. doi:10.1016/j.geoderma.2007.02.004.

Brodowski, S., Rodionov, A., Haumaier, L., Glaser, B., and Amelung, W. (2005). Revised black carbon assessment using benzene polycarboxylic acids. *Org. Geochem.* 36, 1299–1310. doi:10.1016/j.orggeochem.2005.03.011.

Bucheli, T. D., Blum, F., Desaules, A., and Gustafsson, O. (2004). Polycyclic aromatic hydrocarbons, black carbon, and molecular markers in soils of Switzerland. *Chemosphere* 56, 1061–76. doi:10.1016/j.chemosphere.2004.06.002.

Caria, G., Arrouays, D., Dubromel, E., Jolivet, C., Ratié, C., Bernoux, M., et al. (2011). Black carbon estimation in French calcareous soils using chemo-thermal oxidation method. *Soil Use Manag.* 27, 333–339. doi:10.1111/j.1475-2743.2011.00349.x.

Cusack, D. F., Chadwick, O. a., Hockaday, W. C., and Vitousek, P. M. (2012). Mineralogical controls on soil black carbon preservation. *Global Biogeochem. Cycles* 26. doi:10.1029/2011GB004109.

Czimczik, C. I., Preston, C. M., Schmidt, M. W. I., and Schulze, E.-D. (2003). How surface fire in Siberian Scots pine forests affects soil organic carbon in the forest floor: Stocks, molecular structure, and conversion to black carbon (charcoal). *Global Biogeochem. Cycles* 17. doi:10.1029/2002GB001956.

Dai, X., Boutton, T. W., Glaser, B., Ansley, R. J., and Zech, W. (2005). Black carbon in a temperate mixed-grass savanna. *Soil Biol. Biochem.* 37, 1879–1881. doi:10.1016/j.soilbio.2005.02.021.

Eckmeier, E., Gerlach, R., and Skjemstad, J. (2007). Minor changes in soil organic carbon and charcoal concentrations detected in a temperate deciduous forest a year after an experimental slash-and-burn. *Biogeosciences* 4, 377–383. Available at: http://hal.archives-ouvertes.fr/hal-00297620/ [Accessed May 16, 2012].

Glaser, B., and Amelung, W. (2003). Pyrogenic carbon in native grassland soils along a climosequence in North America. *Global Biogeochem. Cycles* 17. doi:10.1029/2002GB002019.

Glaser, B., Balashov, E., Haumaier, L., Guggenberger, G., and Zech, W. (2000). Black carbon in density fractions of anthropogenic soils of the Brazilian Amazon region. *Org. Geochem.* 31, 669–678. doi:10.1016/S0146-6380(00)00044-9.

Hammes, K., Torn, M. S., Lapenas, a. G., and Schmidt, M. W. I. (2008). Centennial black carbon turnover observed in a Russian steppe soil. *Biogeosciences Discuss.* 5, 661–683. doi:10.5194/bgd-5-661-2008.

Van den Heuvel, H., Le Couriaut, T., McMullen, B. M., Lozac'h, F., and Van Noort, P. (2005). Maximum capacities for adsorption of phenantrene in the slowly and very slowly desorbing domains in nineteen soils and sediments. *Environ. Toxicol. Chem.* 24, 830–835.

Hopmans, P., Bauhus, J., Khanna, P., and Weston, C. (2005). Carbon and nitrogen in forest soils: Potential indicators for sustainable management of eucalypt forests in south-eastern Australia. *For. Ecol. Manage.* 220, 75–87. doi:10.1016/j.foreco.2005.08.006.

Jauss, V., Johnson, M., Krull, E., Daub, M., and Lehmann, J. (2015). Pyrogenic carbon controls across a soil catena in the Pacific Northwest. *Catena* 124, 53–59. doi:10.1016/j.catena.2014.09.001.

Kaal, J., and Van Mourik, J. M. (2008). Micromorphological evidence of black carbon in colluvial soils from NW Spain. *Eur. J. Soil Sci.* 59, 1133–1140. doi:10.1111/j.1365-2389.2008.01084.x.

Knicker, H., Wiesmeier, M., and Dick, D. P. (2008). A simplified method for the quantification of pyrogenic organic matter in grassland soils via chemical oxidation. *Geoderma* 147, 69–74. doi:10.1016/j.geoderma.2008.07.008.

Liang, B., Lehmann, J., Solomon, D., Sohi, S., Thies, J. E., Skjemstad, J. O., et al. (2008). Stability of biomass-derived black carbon in soils. *Geochim. Cosmochim. Acta* 72, 6069–6078. doi:10.1016/j.gca.2008.09.028.

Llorente, M., Glaser, B., and Turrión, M. B. (2010). Storage of organic carbon and Black carbon in density fractions of calcareous soils under different land uses. *Geoderma* 159, 31–38. doi:10.1016/j.geoderma.2010.06.011.

McFarlane, K. J., Torn, M. S., Hanson, P. J., Porras, R. C., Swanston, C. W., Callaham, M. a., et al. (2012). Comparison of soil organic matter dynamics at five temperate deciduous forests with physical fractionation and radiocarbon measurements. *Biogeochemistry* 112, 457–476. doi:10.1007/s10533-012-9740-1.

Nam, J. J., Gustafsson, O., Kurt-Karakus, P., Breivik, K., Steinnes, E., and Jones, K. C. (2008). Relationships between organic matter, black carbon and persistent organic pollutants in European background soils: Implications for sources and environmental fate. *Environ. Pollut.* 156, 809–817. doi:10.1016/j.envpol.2008.05.027.

Nguyen, B. T., Lehmann, J., Kinyangi, J., Smernik, R., Riha, S. J., and Engelhard, M. H. (2008). Long-term black carbon dynamics in cultivated soil. *Biogeochemistry* 89, 295–308. doi:10.1007/s10533-008-9220-9.

Paroissien, J. B., Orton, T. G., Saby, N. P. a, Martin, M. P., Jolivet, C. C., Ratie, C., et al. (2012). Mapping black carbon content in topsoils of central France. *Soil Use Manag.* 28, 488–496. doi:10.1111/j.1475-2743.2012.00452.x.

Poirier, N., Derenne, S., Balesdent, J., Rouzaud, J.-N., Mariotti, A., and Largeau, C. (2002). Abundance and composition of the refractory organic fraction of an ancient, tropical soil (Pointe Noire, Congo). *Org. Geochem.* 33, 383–391. doi:10.1016/S0146-6380(01)00168-1.

Quénéa, K., Derenne, S., Rumpel, C., Rouzaud, J. N., Gustafsson, O., Carcaillet, C., et al. (2006). Black carbon yields and types in forest and cultivated sandy soils (Landes de Gascogne, France) as determined with different methods: Influence of change in land use. *Org. Geochem.* 37, 1185–1189. doi:10.1016/j.orggeochem.2006.05.010.

Rivas, Y., Matus, F., Rumpel, C., Knicker, H., and Garrido, E. (2012). Black carbon contribution in volcanic soils affected by wildfire or stubble burning. *Org. Geochem.* 47, 41–50. doi:10.1016/j.orggeochem.2012.03.007.

Rodionov, A., Amelung, W., Haumaier, L., Urusevskaja, I., and Zech, W. (2006). Black carbon in the zonal steppe soils of Russia. *J. Plant Nutr. Soil Sci.* 169, 363–369. doi:10.1002/jpln.200521813.

Rodionov, A., Amelung, W., Peinemann, N., Haumaier, L., Zhang, X., Kleber, M., et al. (2010). Black carbon in grassland ecosystems of the world. *Global Biogeochem. Cycles* 24, 1–15. doi:10.1029/2009GB003669.

Rodionow, A., Flessa, H., Kazansky, O., and Guggenberger, G. (2006). Organic matter composition and potential trace gas production of permafrost soils in the forest tundra in northern Siberia. *Geoderma* 135, 49–62. doi:10.1016/j.geoderma.2005.10.008.

Roth, P. J., Lehndorff, E., Brodowski, S., Bornemann, L., Sanchez-García, L., Gustafsson, O., et al. (2012). Differentiation of charcoal, soot and diagenetic carbon in soil: Method comparison and perspectives. *Org. Geochem.* 46, 66–75. doi:10.1016/j.orggeochem.2012.01.012.

Rovira, P., Duguy, B., and Ramón Vallejo, V. (2009). Black carbon in wildfire-affected shrubland Mediterranean soils. *J. Plant Nutr. Soil Sci.* 172, 43–52. doi:10.1002/jpln.200700216.

Rumpel, C., Alexis, M., Chabbi, a., Chaplot, V., Rasse, D. P., Valentin, C., et al. (2006). Black carbon contribution to soil organic matter composition in tropical sloping land under slash and burn agriculture. *Geoderma* 130, 35–46. doi:10.1016/j.geoderma.2005.01.007.

Schmid, E.-M., Skjemstad, J. ., Glaser, B., Knicker, H., and Kögel-Knabner, I. (2002). Detection of charred organic matter in soils from a Neolithic settlement in Southern Bavaria, Germany. *Geoderma* 107, 71–91. doi:10.1016/S0016-7061(01)00139-2.

Schmidt, M. W. I., Skjemstad, J. O., Gehrt, E., and Ko, I. (1999). Charred organic carbon in German chernozemic soils. *Eur. J. Soil Sci.* 50, 351–365.

Schmidt, M. W. I., Skjemstad, J. O., and Jäger, C. (2002). Carbon isotope geochemistry and nanomorphology of soil black carbon: Black chernozemic soils in central Europe originate from ancient biomass burning. *Global Biogeochem. Cycles* 16, 70–1–70–8. doi:10.1029/2002GB001939.

Schulze, E., Lloyd, J., Kelliher, F. M., Wirth, C., Rebmann, C., Lu, B., et al. (1999). Productivity of forests in the Eurosiberian boreal region and their potential to act as a carbon sink - a synthesis. *Glob. Chang. Biol.*

Shindo, H., Honna, T., Yamamoto, S., and Honma, H. (2004). Contribution of charred plant fragments to soil organic carbon in Japanese volcanic ash soils containing black humic acids. *Org. Geochem.* 35, 235–241. doi:10.1016/j.orggeochem.2003.11.001.

Simpson, M. J., and Hatcher, P. G. (2004). Determination of black carbon in natural organic matter by chemical oxidation and solid-state 13C nuclear magnetic resonance spectroscopy. *Org. Geochem.* 35, 923–935. doi:10.1016/j.orggeochem.2004.04.004.

Skjemstad, J. O., Dalal, R. C., Janik, L. J., and McGowan, J. A. (2001). Changes in chemical nature of soil organic carbon in Vertisols under wheat in south-east Queensland. *Aust. J. Soil Res.* 39, 343–359.

Skjemstad, J. O., Reicosky, D. C., Wilts, A. R., and McGowan, J. A. (2002). Charcoal Carbon in US Agricultural Soils. *Soil Sci. Soc. Am. J.* 66, 1249–1255.

Skjemstad, J. O., Taylor, J. A., Janik, L. J., and Marvanek, S. P. (1999). Soil organic carbon dynamics under long-term sugarcane monoculture. *Aust. J. Soil Res.* 37.

Song, J., Peng, P., and Huang, W. (2002). Black Carbon and Kerogen in Soils. *Environ. Sci. Technol.* 36, 3960–3967.

Soucémarianadin, L. N., Quideau, S. a., and MacKenzie, M. D. (2014). Pyrogenic carbon stocks and storage mechanisms in podzolic soils of fire-affected Quebec black spruce forests. *Geoderma* 217-218, 118–128. doi:10.1016/j.geoderma.2013.11.010.

Wiedemeier, D. B., Hilf, M. D., Smittenberg, R. H., Haberle, S. G., and Schmidt, M. W. I. (2013). Improved assessment of pyrogenic carbon quantity and quality in environmental samples by high-performance liquid chromatography. *J. Chromatogr. A* 1304, 246–50.

Yang, Y., Mahler, B. J., Van Metre, P. C., Ligouis, B., and Werth, C. J. (2010). Potential contributions of asphalt and coal tar to black carbon quantification in urban dust, soils, and sediments. *Geochim. Cosmochim. Acta* 74, 6830–6840. doi:10.1016/j.gca.2010.08.041.

Zhan, C., Cao, J., Han, Y., Huang, S., Tu, X., Wang, P., et al. (2013). Spatial distributions and sequestrations of organic carbon and black carbon in soils from the Chinese loess plateau. *Sci. Total Environ.* 465, 255–266. doi:10.1016/j.scitotenv.2012.10.113.

Supplement Manuscript 1:

Pyrogenic Carbon in Soils: A Literature-Based Inventory and a Global Estimation of Its Content in Soil Organic Carbon and Stocks

Reisser, Moritz, Purves, Ross S., Schmidt, Michael W.I., Abiven, Samuel*

Department of Geography, University of Zurich, Winterthurerstrasse 190, 8057, Zurich, Switzerland

*Corresponding author: samuel.abiven@geo.uzh.ch

reference	Latitude [°]	Longitude [°]	Altitude [m.a.s.l.]	land use	MAP [mm yr-1]	MAT [°C]	KG climate	top or subsoil	BDD [g cm-3]	SOC [%]	clay content [%]	pH	fire frequency	method	fire return interval [yr]	Pyrome	PyC [wt % of SOC]
(Agarwal and Bucheli, 2011)	28.6	77.2	0-500	urban	790	25.1	C	complete	NA	1.65	NA	NA	NA	CTO 375	1 to 30	2	12
	28.6	77.2	0-500	agriculture	790	25.1	C	complete	NA	0.8	NA	NA	NA	CTO 375	1 to 30	2	14.5
	28.6	77.2	0-500	grass	790	25.1	C	complete	NA	0.85	NA	NA	NA	CTO 375	1 to 30	2	14.5
	47	8	0-500	agriculture	1250	8	C	complete	NA	2.5	NA	NA	NA	CTO 375	NA	NA	4
	47	8	0-500	grass	1250	8	C	complete	NA	4	NA	NA	NA	CTO 375	>100	NA	3.8
	47	8	0-500	forest	1250	8	C	complete	NA	4	NA	NA	NA	CTO 375	<1	NA	3.2
	47	8	0-500	grass	1250	8	C	complete	NA	5.5	NA	NA	NA	CTO 375	<1	NA	2.6
	47	8	0-500	forest	1250	8	C	complete	NA	7.1	NA	NA	NA	CTO 375	1 to 30	NA	2.3
	46.32	6.97	0-500	agriculture	1379	10.1	C	complete	NA	0.5	NA	4.6	NA	CTO 375	30 to 100	NA	14
	46.77	6.64	0-500	urban	1150	11	C	complete	NA	35	NA	4.5	NA	CTO 375	1 to 30	NA	6
	47.7	8.63	0-500	forest	863	7.8	C	complete	NA	1.5	NA	4.5	NA	CTO 375	1 to 30	NA	7
(Andreeva et al., 2011)	52.33	109.79	500-1000	NA	250	-5	D	topsoil	NA	NA	NA	NA	NA	BPCA	30 to 100	4	32.9
	52.5	111.53	500-1000	grass	300	-5	D	topsoil	NA	NA	NA	NA	NA	BPCA	30 to 100	4	40.3
(Ansley et al., 2006)	34	-99.33	0-500	grass	665	16.9	C	subsoil	NA	0.77	43	4.4	NA	UV Oxidation	1 to 30	2	14
	34	-99.33	0-500	grass	665	16.9	C	topsoil	NA	1.27	32	3.9	high	UV Oxidation	<1	2	14
	34	-99.33	0-500	grass	665	16.9	C	topsoil	NA	0.98	32	4.8	high	UV Oxidation	30 to 100	2	17
	34	-99.33	0-500	grass	665	16.9	C	subsoil	NA	0.77	43	5.5	high	UV Oxidation	30 to 100	2	16
	34	-99.33	0-500	grass	665	16.9	C	subsoil	NA	0.81	43	5.5	high	UV Oxidation	30 to 100	2	13
	34	-99.33	0-500	grass	665	16.9	C	topsoil	NA	0.94	32	4.4	NA	UV Oxidation	30 to 100	2	13

	40	105	>2000	forest	NA	NA	B	subsoil	NA	1.32	NA	NA	medium	BPCA	<1	NA	3.18
	40	105	>2000	forest	NA	NA	B	topsoil	NA	3.09	NA	NA	medium	BPCA	<1	NA	3.18
	40	105	>2000	forest	NA	NA	B	topsoil	NA	2.32	NA	NA	medium	BPCA	<1	NA	2.95
	40	105	>2000	forest	NA	NA	B	subsoil	NA	1.72	NA	NA	medium	BPCA	<1	NA	2.27
(Brodowski et	-3.6	-55.03	0-500	forest	2050	26.5	A	topsoil	NA	1.44	NA	NA	NA	BPCA	30 to 100	NA	4.49
al., 2005)	49.7	43.65	0-500	NA	300	6	D	subsoil	NA	2.29	NA	NA	NA	BPCA	30 to 100	5	14.8
	51.64	36.18	0-500	grass	573	5.3	D	topsoil	NA	5.64	NA	8.1	NA	BPCA	30 to 100	2	11.19
(Brodowski et	48.36	13.2	0-500	agriculture	890	8.2	C	subsoil	NA	0.31	NA	5.5	NA	BPCA	<1	NA	12.42
al., 2007)	48.36	13.2	0-500	agriculture	890	8.2	C	subsoil	NA	0.52	NA	6.6	NA	BPCA	<1	NA	8.54
	48.36	13.2	0-500	agriculture	890	8.2	C	subsoil	NA	1.31	NA	6.7	NA	BPCA	<1	NA	4.2
	48.36	13.2	0-500	agriculture	890	8.2	C	subsoil	NA	0.77	NA	6.6	NA	BPCA	<1	NA	6.79
	48.36	13.2	0-500	agriculture	890	8.2	C	topsoil	NA	2.5	NA	5.7	NA	BPCA	<1	NA	2.68
	51.37	11.83	0-500	agriculture	480	8.7	C	subsoil	NA	0.14	NA	6.8	NA	BPCA	1 to 30	2	31.47
	51.37	11.83	0-500	agriculture	480	8.7	C	subsoil	NA	0.32	NA	6.8	NA	BPCA	1 to 30	2	19.63
	51.37	11.83	0-500	agriculture	480	8.7	C	topsoil	NA	2.04	NA	NA	NA	BPCA	<1	2	14.22
	51.37	11.83	0-500	agriculture	480	8.7	C	subsoil	NA	1.89	NA	NA	NA	BPCA	1 to 30	2	13.58
	51.37	11.83	0-500	agriculture	480	8.7	C	subsoil	NA	1.84	NA	NA	NA	BPCA	1 to 30	2	13.17
	51.37	11.83	0-500	agriculture	480	8.7	C	subsoil	NA	1.05	NA	NA	NA	BPCA	1 to 30	2	13.11
	51.37	11.29	0-500	agriculture	480	8.8	C	subsoil	NA	0.21	NA	6.4	NA	BPCA	<1	NA	23.81
	51.37	11.29	0-500	agriculture	480	8.8	C	subsoil	NA	0.23	NA	6.4	NA	BPCA	<1	NA	25.22
	51.37	11.29	0-500	agriculture	480	8.8	C	subsoil	NA	0.27	NA	7.3	NA	BPCA	<1	NA	13.53
	51.37	11.29	0-500	agriculture	480	8.8	C	subsoil	NA	0.44	NA	7.1	NA	BPCA	<1	NA	13.18
	51.37	11.29	0-500	agriculture	480	8.8	C	topsoil	NA	1.33	NA	6.8	NA	BPCA	<1	NA	12.14
	51.37	11.29	0-500	agriculture	480	8.8	C	subsoil	NA	0.9	NA	7.1	NA	BPCA	<1	NA	10.52

	51.48	11.97	0-500	agriculture	490	9	C	subsoil	NA	0.11	NA	5.7	NA	BPCA	1 to 30	2	50
	51.48	11.97	0-500	agriculture	490	9	C	subsoil	NA	0.26	NA	5.6	NA	BPCA	1 to 30	2	19.77
	51.48	11.97	0-500	agriculture	490	9	C	subsoil	NA	0.57	NA	7.6	NA	BPCA	1 to 30	2	13.27
	51.48	11.97	0-500	agriculture	490	9	C	subsoil	NA	0.53	NA	5.6	NA	BPCA	1 to 30	2	12.92
	51.48	11.97	0-500	agriculture	490	9	C	subsoil	NA	1.31	NA	7	NA	BPCA	1 to 30	2	12.61
	51.48	11.97	0-500	agriculture	490	9	C	subsoil	NA	0.42	NA	5.8	NA	BPCA	1 to 30	2	12.5
	51.48	11.97	0-500	agriculture	490	9	C	topsoil	NA	1.44	NA	7	NA	BPCA	1 to 30	2	11.92
	51.48	11.97	0-500	agriculture	490	9	C	subsoil	NA	1.24	NA	7.6	NA	BPCA	1 to 30	2	11.74
(Bucheli et al., 2004)	46.01	8.86	1000-1500	forest	NA	9.2	D	topsoil	NA	12.96	NA	4.4	NA	CTO 375	30 to 100	NA	1.39
	46.15	8.98	0-500	urban	NA	10.6	C	topsoil	NA	2.28	NA	5.7	NA	CTO 375	30 to 100	NA	6.58
	46.25	6.28	500-1000	forest	NA	9.2	C	topsoil	NA	3.12	NA	5.5	NA	CTO 375	<1	NA	1.6
	46.27	7.87	500-1000	forest	NA	8.2	C	topsoil	NA	6.63	NA	7.2	NA	CTO 375	<1	NA	2.41
	46.58	8.5	>2000	urban	NA	-0.2	D	topsoil	NA	8.77	NA	5.2	NA	CTO 375	<1	NA	1.71
	46.72	6.53	500-1000	forest	NA	8.3	C	topsoil	NA	4.72	NA	5.5	NA	CTO 375	<1	NA	1.27
	46.8	9.83	1500-2000	forest	NA	2.6	D	topsoil	NA	22.73	NA	5.2	NA	CTO 375	<1	NA	0.75
	46.82	8.65	0-500	grass	NA	8.6	C	topsoil	NA	5.46	NA	5.9	NA	CTO 375	<1	NA	2.01
	46.98	6.61	1000-1500	grass	NA	4.8	D	topsoil	NA	8.86	NA	6.3	NA	CTO 375	<1	NA	1.92
	47.05	9.45	500-1000	forest	NA	6.7	C	topsoil	NA	6.65	NA	5.7	NA	CTO 375	<1	NA	1.35
	47.05	7.47	500-1000	agriculture	NA	7.7	C	topsoil	NA	1.07	NA	3.9	NA	CTO 375	<1	NA	3.74
	47.07	8.43	1000-1500	grass	NA	7.2	D	topsoil	NA	2.18	NA	4.5	NA	CTO 375	<1	NA	6.42

	47.07	7.27	0-500	forest	NA	9.4	C	topsoil	NA	4.67	NA	7	NA	CTO 375	<1	NA	33.62
	47.2	7.43	1000-1500	forest	NA	5.3	D	topsoil	NA	5.71	NA	5.9	NA	CTO 375	<1	NA	2.28
	47.22	7.79	500-1000	forest	NA	8.1	C	topsoil	NA	11.38	NA	NA	NA	CTO 375	<1	NA	0.97
	47.32	9.57	0-500	agriculture	NA	8	C	topsoil	NA	14.6	NA	5.5	NA	CTO 375	<1	NA	2.53
	47.39	8.57	500-1000	forest	NA	7.9	C	topsoil	NA	3.58	NA	NA	NA	CTO 375	<1	NA	1.96
	47.4	8.18	0-500	forest	NA	8.3	C	topsoil	NA	2.85	NA	7.1	NA	CTO 375	<1	NA	3.16
	47.45	8.75	0-500	grass	NA	8.5	C	topsoil	NA	8.09	NA	4	NA	CTO 375	<1	NA	1.11
	47.48	8.91	500-1000	grass	NA	7.1	C	topsoil	NA	4.42	NA	NA	NA	CTO 375	<1	NA	3.85
	47.5	8.75	0-500	urban	NA	7.1	C	topsoil	NA	2.25	NA	4.7	NA	CTO 375	<1	NA	5.33
	47.53	7.57	500-1000	agriculture	NA	9	C	topsoil	NA	1.04	NA	NA	NA	CTO 375	<1	NA	4.81
	49.89	7.28	1000-1500	urban	NA	5.4	D	topsoil	NA	5.4	NA	4.8	NA	CTO 375	<1	NA	2.59
(Caria et al., 2011)	50	2.3	0-500	NA	610	11	C	topsoil	NA	1.29	NA	4.6	NA	CTO 375	<1	NA	62.48
	50	2.3	0-500	NA	610	11	C	topsoil	NA	1.22	NA	4.6	NA	CTO 375	<1	NA	48.2
	50	2.3	0-500	NA	610	11	C	topsoil	NA	0.87	NA	4.6	NA	CTO 375	<1	NA	41.26
	50	2.3	0-500	NA	610	11	C	topsoil	NA	2.58	NA	4.6	NA	CTO 375	<1	NA	39.11
	50	2.3	0-500	NA	610	11	C	topsoil	NA	2.05	NA	4.6	NA	CTO 375	<1	NA	38.44
	50	2.3	0-500	NA	610	11	C	topsoil	NA	3.02	NA	4.6	NA	CTO 375	<1	NA	34.14
	50	2.3	0-500	NA	610	11	C	topsoil	NA	1.38	NA	NA	NA	CTO 375	<1	NA	34.06
	50	2.3	0-500	NA	610	11	C	topsoil	NA	2.2	NA	4.6	NA	CTO 375	<1	NA	33.59
	50	2.3	0-500	NA	610	11	C	topsoil	NA	1.3	NA	NA	NA	CTO 375	<1	NA	32.92
	50	2.3	0-500	NA	610	11	C	topsoil	NA	1.26	NA	NA	NA	CTO 375	<1	NA	31.98
	50	2.3	0-500	NA	610	11	C	topsoil	NA	4.6	NA	4.5	NA	CTO 375	<1	NA	31.41

	50	2.3	0-500	NA	610	11	C	topsoil	NA	2.62	NA	NA	NA	CTO 375	NA	NA	15.8
	50	2.3	0-500	NA	610	11	C	topsoil	NA	2.97	NA	4.6	NA	CTO 375	<1	NA	13.3
	50	2.3	0-500	NA	610	11	C	topsoil	NA	3.59	NA	NA	NA	CTO 375	<1	NA	10.28
(Cusack et al., 2012)	20	-156	1500-2000	grass	2000	NA	A	topsoil	0.4	6.38	NA	NA	NA	NMR	<1	NA	10.56
	20	-156	500-1000	grass	1272	NA	A	topsoil	0.67	1.39	NA	NA	NA	NMR	30 to 100	NA	11.52
	20	-156	500-1000	grass	1865	NA	A	topsoil	0.43	9.23	NA	NA	NA	NMR	<1	NA	12.04
	20	-156	1000-1500	grass	1300	NA	A	topsoil	0.54	12.79	NA	NA	NA	NMR	<1	NA	12.36
	20	-156	0-500	grass	851	NA	A	topsoil	0.8	4.6	NA	5.7	NA	NMR	<1	NA	12.55
	20	-156	500-1000	grass	1983	NA	A	topsoil	0.41	12.08	NA	6.35	NA	NMR	<1	NA	12.74
	20	-156	500-1000	grass	1548	NA	A	topsoil	0.49	8.84	NA	7.21	NA	NMR	<1	NA	13.08
	20	-156	500-1000	grass	1689	NA	A	topsoil	0.55	11.25	NA	6.59	NA	NMR	<1	NA	13.47
	20	-156	500-1000	grass	898	NA	A	topsoil	0.79	2.87	NA	NA	NA	NMR	<1	NA	13.83
	20	-156	500-1000	grass	808	NA	A	topsoil	0.81	6.43	NA	NA	NA	NMR	<1	NA	14.27
	20	-156	500-1000	grass	1103	NA	A	topsoil	0.72	6.19	NA	7.77	NA	NMR	<1	NA	14.37
	20	-156	1000-1500	grass	2400	NA	A	topsoil	0.33	13.74	NA	NA	NA	NMR	<1	NA	14.49
	20	-156	1000-1500	grass	1700	NA	A	topsoil	0.54	11.9	NA	NA	NA	NMR	<1	NA	14.65
	20	-156	500-1000	grass	1103	NA	A	topsoil	0.72	6.8	NA	NA	NA	NMR	30 to 100	NA	14.87
	20	-156	500-1000	grass	1197	NA	A	topsoil	0.7	6.77	NA	7.02	NA	NMR	<1	NA	14.92
	20	-156	0-500	grass	967	NA	A	topsoil	0.61	5.48	NA	7.69	NA	NMR	<1	NA	15.34
	20	-156	500-1000	grass	1272	NA	A	topsoil	0.67	8.59	NA	7.05	NA	NMR	<1	NA	15.36

		1000-														
20	-156	1500	grass	1900	NA	A	topsoil	0.48	10.6	NA	NA	NA	NMR	<1	NA	15.78
20	-156	500-1000	NA	615	NA	A	topsoil	0.87	2.67	NA	NA	NA	NMR	<1	NA	16.04
20	-156	500-1000	grass	1103	NA	A	topsoil	0.72	6.2	NA	6.15	NA	NMR	<1	NA	16.11
20	-156	500-1000	grass	830	NA	A	topsoil	0.81	7.46	NA	6.82	NA	NMR	<1	NA	16.24
		1000-														
20	-156	1500	grass	1100	NA	A	topsoil	0.58	11.48	NA	7.04	NA	NMR	<1	NA	16.24
20	-156	0-500	grass	1113	NA	A	topsoil	0.72	1.96	NA	NA	NA	NMR	<1	NA	16.92
20	-156	500-1000	grass	1944	NA	A	topsoil	0.47	11.97	NA	6.45	NA	NMR	<1	NA	17.36
20	-156	500-1000	grass	1197	NA	A	topsoil	0.7	5.82	NA	6.35	NA	NMR	<1	NA	17.48
20	-156	0-500	NA	588	NA	A	topsoil	0.88	2.59	NA	NA	NA	NMR	<1	NA	17.53
		1000-														
20	-156	1500	grass	1000	NA	A	topsoil	0.6	16.32	NA	6.63	NA	NMR	<1	NA	17.75
20	-156	500-1000	grass	1763	NA	A	topsoil	0.45	11.86	NA	6.59	NA	NMR	<1	NA	17.89
20	-156	500-1000	grass	1175	NA	A	topsoil	0.57	5.79	NA	NA	NA	NMR	<1	NA	18.34
20	-156	500-1000	grass	1006	NA	A	topsoil	0.75	8.24	NA	6.85	NA	NMR	<1	NA	18.35
20	-156	0-500	grass	800	NA	A	topsoil	0.64	2.4	NA	6.39	NA	NMR	<1	NA	18.36
20	-156	500-1000	NA	675	NA	A	topsoil	0.85	4.46	NA	7.1	NA	NMR	<1	NA	18.82
20	-156	0-500	NA	566	NA	A	topsoil	0.69	2.62	NA	7.05	NA	NMR	<1	NA	18.96
20	-156	500-1000	grass	1272	NA	A	topsoil	0.67	7.67	NA	6.35	NA	NMR	<1	NA	18.97
20	-156	0-500	NA	725	NA	A	topsoil	0.66	4.21	NA	NA	NA	NMR	<1	NA	19.31
20	-156	0-500	grass	851	NA	A	topsoil	0.8	7.52	NA	NA	NA	NMR	<1	NA	19.48
		1000-														
20	-156	1500	grass	1500	NA	A	topsoil	0.5	8.33	NA	6.26	NA	NMR	<1	NA	19.52

	20	-156	500-1000	grass	1272	NA	A	topsoil	0.67	2.04	NA	6.61	NA	NMR	<1	NA	20.94
	20	-156	500-1000	grass	1323	NA	A	topsoil	0.66	10.72	NA	6.6	NA	NMR	<1	NA	22.18
	20	-156	500-1000	grass	1103	NA	A	topsoil	0.72	9.03	NA	NA	NA	NMR	<1	NA	22.47
	20	-156	1000-1500	NA	750	NA	A	topsoil	0.65	8.59	NA	7.19	NA	NMR	<1	NA	22.86
	20	-156	500-1000	NA	690	NA	A	topsoil	0.85	4.47	NA	6.66	NA	NMR	<1	NA	22.95
	20	-156	0-500	NA	261	NA	A	topsoil	0.98	1.52	NA	7.48	NA	NMR	<1	NA	25.37
	20	-156	0-500	NA	220	NA	A	topsoil	0.99	2	NA	6.58	NA	NMR	<1	NA	29.92
(Czimczik et al.,	60.67	89.13	0-500	forest	493	-2.5	D	topsoil	NA	31.06	NA	NA	medium	BPCA	1 to 30	3	4.49
2003)	60.67	89.13	0-500	forest	493	-2.5	D	topsoil	NA	24.81	NA	NA	medium	BPCA	<1	3	0.29
	60.75	89.4	0-500	forest	560	-3	D	complete	NA	NA	NA	4.4	medium	BPCA	30 to 100	3	0.14
	60.75	89.4	0-500	forest	560	-3	D	complete	NA	NA	NA	4.4	low	BPCA	30 to 100	3	0.12
(Dai et al.,	33.85	-99.45	0-500	grass	665	16.9	C	subsoil	NA	0.6	NA	5.5	high	BPCA	30 to 100	2	11.7
2005)	33.85	-99.45	0-500	grass	665	16.9	C	topsoil	NA	0.92	NA	5.8	high	BPCA	30 to 100	2	9.1
	33.85	-99.45	0-500	grass	665	16.9	C	subsoil	NA	0.73	NA	5.9	NA	BPCA	30 to 100	2	7.4
	33.85	-99.45	0-500	grass	665	16.9	C	topsoil	NA	0.89	NA	6.4	NA	BPCA	30 to 100	2	7.2
(Eckmeier et	49.27	9.47	0-500	forest	849	8.9	C	topsoil	NA	3.6	15	NA	NA	UV Oxidation	<1	NA	2.5
al., 2007)	49.27	9.47	0-500	forest	849	8.9	C	topsoil	NA	3.77	15	NA	NA	UV Oxidation	<1	NA	2.7
	49.27	9.47	0-500	forest	849	8.9	C	topsoil	NA	3.79	15	NA	NA	UV Oxidation	<1	NA	2.6
	46.39	9.92	1500-2000	grass	1700	0	E	topsoil	NA	0.32	NA	7.5	NA	BPCA	1 to 30	NA	13.67
	46.39	9.92	1500-2000	grass	1700	0	E	topsoil	NA	2.29	NA	7.5	NA	BPCA	1 to 30	NA	6.14
	46.39	9.92	1500-	grass	1700	0	E	topsoil	NA	1.42	NA	7.5	NA	BPCA	1 to 30	NA	5.81

		2000													
		1500-													
46.39	9.92	2000	grass	1700	0	E	topsoil	NA	0.73	NA	7.5	NA	BPCA	1 to 30	NA	5.45
		1500-													
46.39	9.92	2000	grass	1700	0	E	topsoil	NA	0.6	NA	NA	NA	BPCA	1 to 30	NA	5.01
		1500-													
46.39	9.92	2000	grass	1700	0	E	topsoil	NA	0.94	NA	7.5	NA	BPCA	1 to 30	NA	4.99
		1500-													
46.39	9.92	2000	shrubs	1700	0	E	topsoil	NA	0.71	NA	NA	NA	BPCA	1 to 30	NA	4.97
		1500-													
46.39	9.92	2000	grass	1700	0	E	topsoil	NA	1.81	NA	7.5	NA	BPCA	1 to 30	NA	4.88
		1500-													
46.39	9.92	2000	grass	1700	0	E	topsoil	NA	1.83	NA	NA	NA	BPCA	1 to 30	NA	4.8
		1500-													
46.39	9.92	2000	grass	1700	0	E	topsoil	NA	1.16	NA	7.5	NA	BPCA	1 to 30	NA	4.66
		1500-													
46.39	9.92	2000	grass	1700	0	E	topsoil	NA	0.49	NA	NA	NA	BPCA	1 to 30	NA	4.64
		1500-													
46.39	9.92	2000	grass	1700	0	E	topsoil	NA	4.79	NA	7.5	NA	BPCA	30 to 100	NA	4.49
		1500-													
46.39	9.92	2000	grass	1700	0	E	topsoil	NA	0.53	NA	7.5	NA	BPCA	1 to 30	NA	4.47
		1500-													
46.39	9.92	2000	grass	1700	0	E	topsoil	NA	6.12	NA	7.5	NA	BPCA	>100	NA	4.31
46.39	9.92	1500-	shrubs	1700	0	E	topsoil	NA	6.41	NA	NA	NA	BPCA	1 to 30	NA	4.32

			2000													
			1500-													
	46.39	9.92	2000	grass	1700	0	E	topsoil	NA	13.1	NA	7.5	NA	BPCA	1 to 30	NA	4.28
			1500-													
	46.39	9.92	2000	grass	1700	0	E	topsoil	NA	3.17	NA	7.5	NA	BPCA	1 to 30	NA	4.02
			1500-													
	46.39	9.92	2000	grass	1700	0	E	topsoil	NA	0.93	NA	NA	NA	BPCA	1 to 30	NA	3.56
			1500-													
	46.39	9.92	2000	grass	1700	0	E	topsoil	NA	3.03	NA	7.5	NA	BPCA	1 to 30	NA	3.31
			1500-													
	46.39	9.92	2000	grass	1700	0	E	topsoil	NA	1.26	NA	6.1	NA	BPCA	1 to 30	NA	3.02
			1500-													
	46.39	9.92	2000	grass	1700	0	E	topsoil	NA	3.7	NA	NA	NA	BPCA	1 to 30	NA	2.79
			1500-													
	46.39	9.92	2000	grass	1700	0	E	topsoil	NA	1.15	NA	NA	NA	BPCA	1 to 30	NA	2.71
			1500-													
	46.39	9.92	2000	grass	1700	0	E	topsoil	NA	5.45	NA	NA	NA	BPCA	1 to 30	NA	2.58
			1500-													
	46.39	9.92	2000	grass	1700	0	E	topsoil	NA	8.97	NA	7.5	NA	BPCA	1 to 30	NA	2.59
			1500-													
	46.39	9.92	2000	grass	1700	0	E	topsoil	NA	1.81	NA	NA	NA	BPCA	1 to 30	NA	2.37
			1500-													
	46.39	9.92	2000	grass	1700	0	E	topsoil	NA	6.45	NA	NA	NA	BPCA	<1	NA	2.3
(Glaser and	27.45	-98.04	0-500	NA	700	22.2	C	topsoil	NA	2.25	25.9	4.9	NA	BPCA	30 to 100	2	11.2

Amelung, 2003)	27.57	-98.54	0-500	grass	440	23.4	C	topsoil	NA	1.6	28.4	7.4	NA	BPCA	30 to 100	3	4.63
	29.42	-96.33	0-500	grass	1030	20	C	topsoil	NA	2.37	25.1	5.6	NA	BPCA	1 to 30	2	9.49
	30.05	-94.06	0-500	grass	1308	20.3	C	topsoil	NA	2.37	25.8	6	NA	BPCA	30 to 100	3	8.99
	32.15	-101.28	500-1000	grass	466	17.1	C	topsoil	NA	1.13	20.9	7.1	NA	BPCA	30 to 100	3	6.46
	37.2	-95.16	0-500	grass	1000	14.2	C	topsoil	NA	2.68	18.2	6.2	NA	BPCA	30 to 100	3	8.4
	38.53	-99.2	500-1000	grass	573	12.2	C	topsoil	NA	2.75	27.5	6.1	NA	BPCA	30 to 100	3	5.05
	39.11	-96.35	0-500	grass	791	12.4	C	topsoil	NA	3.07	33.2	6.7	NA	BPCA	30 to 100	2	17.56
	40.1	-103.13	1000-1500	grass	375	10.8	B	topsoil	NA	1.69	17.7	5.9	NA	BPCA	1 to 30	2	4.26
	40.26	-99.22	500-1000	grass	666	11.6	D	topsoil	NA	2.99	24.4	5.9	NA	BPCA	30 to 100	3	7.66
	40.48	-96.42	0-500	grass	792	10.9	D	topsoil	NA	4.05	32.3	5.4	NA	BPCA	30 to 100	3	8.54
	44.5	-105.51	1000-1500	grass	400	7.2	B	topsoil	NA	1.85	23.8	5.6	NA	BPCA	<1	4	12.43
	45.35	-95.55	0-500	grass	565	6.1	D	topsoil	NA	6.4	34.4	NA	NA	BPCA	30 to 100	3	14.17
	46.5	-100.54	500-1000	grass	419	5	D	topsoil	NA	3.16	20.6	7.4	NA	BPCA	30 to 100	4	8.64
	48.33	-109.41	1000-1500	grass	300	6.1	B	topsoil	NA	1.64	16.5	7.2	NA	BPCA	30 to 100	3	3.78
	50.17	-107.5	500-1000	grass	380	3.2	D	topsoil	NA	4.23	2.2	NA	NA	BPCA	<1	NA	6.5
	52.19	-106.17	500-1000	grass	343	1.6	D	topsoil	NA	4.23	16.2	NA	NA	BPCA	30 to 100	3	7.38
	52.92	-105.8	0-500	grass	456	0.9	D	topsoil	NA	5.82	29.1	NA	NA	BPCA	30 to 100	2	11.56
(Glaser et al.,	-3.6	-54.93	0-500	forest	2050	26	A	topsoil	NA	7	NA	5.5	NA	BPCA	30 to 100	NA	31
2000)	-3.6	-54.93	0-500	forest	2050	26	A	topsoil	NA	1.32	NA	3.9	NA	BPCA	30 to 100	NA	18.94
	-3.6	-54.93	0-500	forest	2050	26	A	subsoil	NA	4.57	NA	4.8	NA	BPCA	30 to 100	NA	17.72
	-3.6	-54.93	0-500	forest	2050	26	A	subsoil	NA	2.34	NA	4.4	NA	BPCA	30 to 100	NA	5.56

	-3.25	-60.42	0-500	urban	2050	26	A	subsoil	NA	2.15	NA	NA	NA	BPCA	30 to 100	2	27.91
	-3.25	-60.42	0-500	urban	2050	26	A	topsoil	NA	3.35	NA	NA	NA	BPCA	30 to 100	2	20.3
	-3.25	-60.42	0-500	urban	2050	26	A	topsoil	NA	1.18	NA	5.5	NA	BPCA	30 to 100	2	5.93
	-3.2	-60.4	0-500	urban	2050	26	A	subsoil	NA	0.83	NA	NA	NA	BPCA	30 to 100	2	24.1
	-3.2	-60.4	0-500	urban	2050	26	A	topsoil	NA	3.45	NA	NA	NA	BPCA	30 to 100	2	12.17
	-3.2	-60.4	0-500	urban	2050	26	A	topsoil	NA	1.18	NA	NA	NA	BPCA	30 to 100	2	5.93
	-3.1	-60.35	0-500	urban	2050	26	A	subsoil	NA	0.98	NA	NA	NA	BPCA	30 to 100	2	14.29
	-3.1	-60.35	0-500	urban	2050	26	A	topsoil	NA	3.25	NA	NA	NA	BPCA	30 to 100	2	13.23
	-3.1	-60.35	0-500	urban	2050	26	A	topsoil	NA	1.45	NA	NA	NA	BPCA	30 to 100	2	6.9
	-2.91	-60.05	0-500	urban	2050	26	A	subsoil	NA	1.76	NA	3.9	NA	BPCA	30 to 100	NA	38.07
	-2.91	-60.05	0-500	urban	2050	26	A	topsoil	NA	2.61	NA	4.8	NA	BPCA	30 to 100	NA	18.77
	-2.91	-60.05	0-500	urban	2050	26	A	topsoil	NA	2.47	NA	4.4	NA	BPCA	30 to 100	NA	12.96
(Hammes et al.,	51	40.7	0-500	grass	507	6.6	D	subsoil	0.83	5.57	NA	NA	NA	BPCA	30 to 100	5	30.48
2008)	51	40.7	0-500	grass	507	6.6	D	subsoil	0.91	4.14	NA	NA	NA	BPCA	30 to 100	5	30.1
	51	40.7	0-500	grass	507	6.6	D	subsoil	0.93	4.55	NA	NA	NA	BPCA	30 to 100	5	20.21
	51	40.7	0-500	grass	507	6.6	D	subsoil	0.93	4.4	NA	NA	NA	BPCA	30 to 100	5	20.02
	51	40.7	0-500	grass	507	6.6	D	subsoil	0.94	3.34	NA	NA	NA	BPCA	30 to 100	5	19.57
	51	40.7	0-500	grass	507	6.6	D	topsoil	0.52	7.42	NA	NA	NA	BPCA	30 to 100	5	18.69
	51	40.7	0-500	grass	507	6.6	D	subsoil	0.99	2.88	NA	NA	NA	BPCA	30 to 100	5	18.52
	51	40.7	0-500	grass	507	6.6	D	topsoil	0.77	4.73	NA	NA	NA	BPCA	30 to 100	2	21.16
	51	40.7	0-500	grass	507	6.6	D	subsoil	0.97	3.08	NA	NA	NA	BPCA	30 to 100	5	9.88
	51	40.7	0-500	grass	507	6.6	D	subsoil	1.25	2.6	NA	NA	NA	BPCA	30 to 100	5	6.81
	51	40.7	0-500	grass	507	6.6	D	subsoil	0.95	3.3	NA	NA	NA	BPCA	30 to 100	5	1.65
	51	40.7	0-500	grass	507	6.6	D	subsoil	1.25	2.75	NA	NA	NA	BPCA	30 to 100	5	0.08

(Hopmans et	-37.63	148.84	0-500	forest	1094	15	C	topsoil	NA	NA	NA	NA	NA	physical	>100	2	17.61
al., 2005)	-37.53	146.25	500-1000	forest	1900	4	C	topsoil	NA	NA	NA	6	NA	physical	>100	4	31.58
	-37.53	146.25	500-1000	forest	1900	4	C	topsoil	NA	NA	NA	NA	NA	physical	>100	4	14.74
(Jauss et al.,	44.2	121.4	500-1000	forest	220	8.5	B	complete	NA	NA	NA	NA	medium	UV Oxidation	<1	NA	27.79
2015)			1000-														
	44.35	122.3	1500	forest	2760	6.1	D	complete	NA	NA	NA	NA	low	UV Oxidation	<1	NA	17.02
	44.4	122.35	500-1000	forest	2010	10.3	B	complete	NA	NA	NA	NA	low	UV Oxidation	<1	NA	6.52
			1000-														
	44.4	122	1500	forest	2040	7.6	D	complete	NA	NA	NA	NA	low	UV Oxidation	<1	4	14.28
	44.5	122.25	0-500	forest	1500	10.3	B	complete	NA	NA	NA	NA	low	UV Oxidation	>100	3	17.08
	44.5	121.6	500-1000	forest	1980	8.1	B	complete	NA	NA	NA	NA	medium	UV Oxidation	<1	NA	13.15
	44.6	122.3	0-500	agriculture	1143	11.7	C	complete	NA	NA	NA	NA	medium	UV Oxidation	>100	3	23.25
	44.6	122.3	0-500	agriculture	1143	11.7	C	complete	NA	NA	NA	NA	medium	UV Oxidation	>100	3	7.72
	44.6	122.25	0-500	agriculture	1143	11.7	C	complete	NA	NA	NA	NA	medium	UV Oxidation	>100	3	11.18
	45	123.9	0-500	forest	2510	10.1	C	complete	NA	NA	NA	NA	low	UV Oxidation	30 to 100	4	16.36
	45	123.9	0-500	forest	2510	10.1	C	complete	NA	NA	NA	NA	low	UV Oxidation	30 to 100	4	15.77
(Kaal and Van	42.54	-8.54	0-500	shrubs	1000	14.8	C	subsoil	NA	5.35	NA	NA	NA	physical	30 to 100	1	14.94
Mourik, 2008)	42.54	-8.54	0-500	shrubs	1000	14.8	C	subsoil	NA	2.66	NA	NA	NA	physical	<1	1	11.52
	42.54	-8.54	0-500	shrubs	1000	14.8	C	subsoil	NA	8.74	NA	NA	NA	physical	30 to 100	1	5.77
	42.54	-8.54	0-500	shrubs	1000	14.8	C	subsoil	NA	3.89	NA	NA	NA	physical	30 to 100	1	5.6
	42.54	-8.54	0-500	shrubs	1000	14.8	C	topsoil	NA	6.34	NA	NA	NA	physical	30 to 100	1	4.19
	42.54	-8.54	0-500	shrubs	1000	14.8	C	subsoil	NA	5.3	NA	NA	NA	physical	<1	1	3.98
	42.54	-8.54	0-500	shrubs	1000	14.8	C	subsoil	NA	3.59	NA	NA	NA	physical	30 to 100	1	3.79
	42.54	-8.54	0-500	shrubs	1000	14.8	C	topsoil	NA	4.49	NA	NA	NA	physical	30 to 100	1	2.63

	42.54	-8.54	0-500	shrubs	1000	14.8	C	subsoil	NA	5.34	NA	NA	NA	physical	30 to 100	1	2.68
	42.54	-8.54	0-500	shrubs	1000	14.8	C	topsoil	NA	9.1	NA	NA	NA	physical	>100	1	1.6
	42.54	-8.54	0-500	shrubs	1000	14.8	C	topsoil	NA	8.05	NA	NA	NA	physical	30 to 100	1	0.9
	42.54	-8.54	0-500	shrubs	1000	14.8	C	subsoil	NA	11.98	NA	NA	NA	physical	30 to 100	1	0.61
(Knicker et al.,	-28.25	-52.4	500-1000	NA	1800	17.7	C	subsoil	NA	6.4	NA	NA	high	Cr2O6	1 to 30	3	50.03
2008)	-28.25	-52.4	500-1000	NA	1800	17.7	C	subsoil	NA	9.8	NA	NA	high	Cr2O6	1 to 30	3	46.26
	-28.25	-52.4	500-1000	NA	1800	17.7	C	topsoil	NA	7.8	NA	NA	high	Cr2O6	1 to 30	3	44.37
	-28.25	-52.4	500-1000	NA	1800	17.7	C	topsoil	NA	12.1	NA	NA	high	Cr2O6	1 to 30	3	42.48
	-28.68	-49.85	1000-1500	grass	2468	14.4	B	subsoil	0.73	6.3	NA	7.1	NA	Cr2O6	1 to 30	5	14
	-28.68	-49.85	1000-1500	grass	2468	14.4	B	subsoil	0.9	4.9	NA	NA	NA	Cr2O6	30 to 100	5	14
	-28.68	-49.85	1000-1500	grass	2468	14.4	B	subsoil	0.73	9.4	NA	NA	NA	Cr2O6	1 to 30	5	9
	-28.68	-49.85	1000-1500	grass	2468	14.4	B	subsoil	0.83	6.8	NA	NA	NA	Cr2O6	1 to 30	5	9
	-28.68	-49.85	1000-1500	grass	2468	14.4	B	topsoil	0.73	13.7	NA	7.1	NA	Cr2O6	1 to 30	5	9
	-28.68	-49.85	1000-1500	grass	2468	14.4	B	subsoil	0.73	10.8	NA	NA	NA	Cr2O6	1 to 30	5	8
	-28.68	-49.85	1000-1500	grass	2468	14.4	B	subsoil	0.64	11	NA	NA	NA	Cr2O6	1 to 30	5	8
	-28.68	-49.85	1000-1500	grass	2468	14.4	B	subsoil	0.64	8	NA	7.1	NA	Cr2O6	1 to 30	5	8

	-28.68	-49.85	1000-1500	grass	2468	14.4	B	subsoil	0.9	6.4	NA	7.1	NA	Cr2O6	1 to 30	5	8
	-28.68	-49.85	1000-1500	grass	2468	14.4	B	subsoil	0.9	6.2	NA	NA	NA	Cr2O6	1 to 30	5	8
	-28.68	-49.85	1000-1500	grass	2468	14.4	B	subsoil	0.83	7.7	NA	NA	NA	Cr2O6	1 to 30	5	7
	-28.68	-49.85	1000-1500	grass	2468	14.4	B	topsoil	0.64	15.1	NA	7.1	NA	Cr2O6	<1	5	7
	-28.68	-49.85	1000-1500	grass	2468	14.4	B	topsoil	0.9	8.9	NA	7.1	NA	Cr2O6	<1	5	6
	-28.68	-49.85	1000-1500	grass	2468	14.4	B	topsoil	0.83	11.1	NA	NA	NA	Cr2O6	1 to 30	5	5
	-28.68	-49.85	1000-1500	grass	2468	14.4	B	subsoil	0.83	5.5	NA	NA	NA	Cr2O6	1 to 30	5	12
	-28.68	-49.85	1000-1500	grass	2468	14.4	B	subsoil	0.64	12.7	NA	NA	NA	Cr2O6	1 to 30	5	7
(Liang et al., 2008)	-3.13	-59.87	0-500	NA	2286	26	A	topsoil	NA	1.54	8.5	8.3	NA	NMR	30 to 100	3	44.3
	-3.13	-59.87	0-500	NA	2286	26	A	topsoil	NA	2.18	35.9	8.1	NA	NMR	30 to 100	3	20.2
	-3.13	-59.87	0-500	forest	2286	26	A	topsoil	NA	1.75	26.7	7.9	NA	NMR	30 to 100	3	9.3
	-3.13	-59.87	0-500	forest	2286	26	A	topsoil	NA	1.02	0.3	8.2	NA	NMR	30 to 100	3	10.6
(Llorente et al., 2010)	41.9	-4.4	500-1000	agriculture	390	12.3	C	topsoil	NA	1.59	30	NA	NA	BPCA	1 to 30	3	23.09
	41.9	-4.4	500-1000	agriculture	390	12.3	C	topsoil	NA	2.78	30	8	NA	BPCA	1 to 30	3	20.83
	41.9	-4.4	500-1000	forest	390	12.3	C	topsoil	NA	6.51	30	NA	NA	BPCA	1 to 30	3	20.79
	41.9	-4.4	500-1000	forest	390	12.3	C	topsoil	NA	5.42	30	NA	NA	BPCA	1 to 30	3	19.34

	41.9	-4.4	500-1000	forest	390	12.3	C	topsoil	NA	3.7	30	NA	NA	BPCA	1 to 30	3	17.59
	41.9	-4.4	500-1000	forest	390	12.3	C	topsoil	NA	5.45	30	NA	NA	BPCA	1 to 30	3	17.21
	41.9	-4.4	500-1000	forest	390	12.3	C	topsoil	NA	5.87	30	NA	NA	BPCA	1 to 30	3	15.17
	41.9	-4.4	500-1000	agriculture	390	12.3	C	topsoil	NA	1.56	30	NA	NA	BPCA	1 to 30	3	12.18
	41.9	-4.4	500-1000	forest	390	12.3	C	topsoil	NA	3.47	30	NA	NA	BPCA	1 to 30	3	10.64
(McFarlane et	41.45	-124.05	0-500	forest	1709	11	C	topsoil	NA	NA	1	NA	NA	BPCA	<1	NA	9.08
al., 2012)	41.45	-124.05	0-500	forest	1709	11	C	subsoil	NA	NA	2	NA	NA	BPCA	<1	NA	13.62
	41.45	-124.05	0-500	forest	1709	11	C	subsoil	NA	NA	3	NA	NA	BPCA	<1	NA	14.76
	41.45	-124.05	0-500	grass	1709	11	C	topsoil	NA	NA	1	NA	high	BPCA	<1	NA	15.89
	41.45	-124.05	0-500	forest	1709	11	C	subsoil	NA	NA	7	8.1	NA	BPCA	<1	NA	15.89
	41.45	-124.05	0-500	grass	1709	11	C	subsoil	NA	NA	1	7.9	high	BPCA	<1	NA	19.3
	41.45	-124.05	0-500	grass	1709	11	C	subsoil	NA	NA	5	7.9	high	BPCA	<1	NA	24.97
	41.45	-124.05	0-500	grass	1709	11	C	subsoil	NA	NA	22	8.1	high	BPCA	<1	NA	27.24
(Nam et al.,	52	-2	0-500	grass	750	10	C	topsoil	NA	10.4	NA	NA	NA	CTO 375	30 to 100	NA	1.03
2008)	52	-2	0-500	forest	750	10	C	topsoil	NA	24.9	NA	NA	NA	CTO 375	30 to 100	NA	0.54
(Nguyen et al.,			1500-														
2008)	0.08	34.98	2000	NA	2000	19	A	topsoil	1.12	2.32	47	NA	NA	NMR	30 to 100	2	28.09
			1500-														
	0.08	34.98	2000	NA	2000	19	A	topsoil	0.8	4.62	47	NA	NA	NMR	30 to 100	2	18.67
			1500-														
	0.08	34.98	2000	NA	2000	19	A	topsoil	1.06	2.58	47	NA	NA	NMR	30 to 100	2	17.19
			1500-														
	0.08	34.98	2000	NA	2000	19	A	topsoil	1.12	1.39	47	NA	NA	NMR	30 to 100	2	16.7
	0.08	34.98	1500-	NA	2000	19	A	topsoil	0.8	6.74	47	NA	NA	NMR	30 to 100	2	15.95

			2000													
			1500-													
	0.08	34.98	2000	NA	2000	19	A	topsoil	0.7	7.56	47	NA	NA	NMR	30 to 100	2	15.5
			1500-													
	0.08	34.98	2000	NA	2000	19	A	topsoil	1	2.74	47	NA	NA	NMR	30 to 100	2	14.78
			1500-													
	0.08	34.98	2000	NA	2000	19	A	topsoil	1.12	1.39	47	NA	NA	NMR	30 to 100	2	10.92
			1500-													
	0.08	34.98	2000	NA	2000	19	A	topsoil	0.67	9.18	47	NA	NA	NMR	30 to 100	2	10.73
(Paroissien et																	
al., 2012)	48	0.8	0-500	NA	650	11	C	topsoil	NA	1.65	17.1	NA	NA	CTO 375	<1	NA	4.85
(Poirier et al.,																	
2002)	-4.78	11.51	0-500	grass	NA	NA	A	subsoil	NA	0.09	8.5	NA	NA	other	<1	NA	5
(Quénéa et al.,	44.74	-0.68	0-500	forest	944	13.8	C	topsoil	NA	2.6	NA	6.37	NA	physical	30 to 100	2	4.6
2006)	44.74	-0.68	0-500	agriculture	944	13.8	C	topsoil	NA	2.6	NA	6.24	NA	physical	30 to 100	2	2.5
(Rivas et al.,			1000-														
2012)	-38.2	-71.83	1500	forest	2500	7	C	topsoil	0.41	8.12	NA	5.2	NA	Cr2O6	30 to 100	4	44.95
			1000-														
	-38.2	-71.83	1500	forest	2500	7	C	topsoil	0.43	9.84	NA	3.9	NA	Cr2O6	30 to 100	4	34.51
			1000-														
	-38.2	-71.83	1500	forest	2500	7	C	subsoil	0.41	8.41	NA	5.4	NA	Cr2O6	30 to 100	4	21.7
			1000-														
	-38.2	-71.83	1500	forest	2500	7	C	subsoil	0.48	6.55	NA	5.1	NA	Cr2O6	30 to 100	4	20.91
	-38.2	-71.83	1000-	forest	2500	7	C	topsoil	0.45	15.68	NA	NA	NA	Cr2O6	30 to 100	4	19.55

		1500														
		1000-1500														
-38.2	-71.83		forest	2500	7	C	subsoil	0.43	10.79	NA	NA	NA	Cr2O6	30 to 100	4	19.41
-38.2	-71.83	1000-1500	forest	2500	7	C	subsoil	0.4	16.29	NA	5	NA	Cr2O6	30 to 100	4	17.12
-38.2	-71.83	1000-1500	forest	2500	7	C	subsoil	0.44	9.66	NA	NA	NA	Cr2O6	30 to 100	4	17.01
-38.2	-71.83	1000-1500	forest	2500	7	C	subsoil	0.46	7.29	NA	NA	NA	Cr2O6	30 to 100	4	16.96
-38.2	-71.83	1000-1500	forest	2500	7	C	subsoil	0.47	7.49	NA	2.6	NA	Cr2O6	30 to 100	4	16.91
-38.2	-71.83	1000-1500	forest	2500	7	C	subsoil	0.52	12.03	NA	5.3	NA	Cr2O6	30 to 100	4	15.58
-38.2	-71.83	1000-1500	forest	2500	7	C	subsoil	0.44	7.88	NA	4.9	NA	Cr2O6	30 to 100	NA	14.28
-38.2	-71.83	1000-1500	forest	2500	7	C	topsoil	0.39	12.11	NA	3.5	NA	Cr2O6	30 to 100	4	13.71
-38.2	-71.83	1000-1500	forest	2500	7	C	subsoil	0.49	10.08	NA	5	NA	Cr2O6	30 to 100	4	12.7
-38.2	-71.83	1000-1500	forest	2500	7	C	subsoil	0.45	5.52	NA	4.9	NA	Cr2O6	30 to 100	4	23.6
-38.2	-71.83	1000-1500	forest	2500	7	C	subsoil	0.44	7.31	NA	3.8	NA	Cr2O6	30 to 100	4	12.42
-36.87	-71.93	0-500	agriculture	1025	14	C	subsoil	0.74	6.65	NA	4.9	NA	Cr2O6	>100	4	34.96

	-36.87	-71.93	0-500	agriculture	1025	14	C	topsoil	0.74	9.48	NA	5.4	NA	Cr2O6	>100	4	30.34
	-36.87	-71.93	0-500	agriculture	1025	14	C	topsoil	0.75	8.58	NA	NA	NA	Cr2O6	>100	4	29.23
	-36.87	-71.93	0-500	agriculture	1025	14	C	subsoil	0.71	3.72	NA	5	NA	Cr2O6	>100	4	25.59
	-36.87	-71.93	0-500	agriculture	1025	14	C	subsoil	0.72	5.61	NA	5.3	NA	Cr2O6	>100	4	18.74
	-36.87	-71.93	0-500	agriculture	1025	14	C	subsoil	0.77	4.11	NA	5.4	NA	Cr2O6	<1	4	17.98
	-36.87	-71.93	0-500	agriculture	1025	14	C	subsoil	0.66	5.94	NA	5.2	NA	Cr2O6	>100	4	17.28
	-36.87	-71.93	0-500	agriculture	1025	14	C	subsoil	0.75	8.02	NA	5.4	NA	Cr2O6	>100	4	14.85
(Rodionov et	47.34	44.5	0-500	agriculture	325	8	D	topsoil	NA	1.59	NA	NA	NA	BPCA	30 to 100	4	8.01
al., 2006)	47.34	44.5	0-500	agriculture	325	8	D	subsoil	NA	0.8	NA	NA	NA	BPCA	30 to 100	4	1.56
	50	44.5	0-500	agriculture	300	6	D	topsoil	NA	3.2	NA	NA	NA	BPCA	30 to 100	3	12.58
	50	44.5	0-500	agriculture	300	6	D	subsoil	NA	1.53	NA	NA	NA	BPCA	30 to 100	2	8.84
	51.75	36.15	0-500	agriculture	573	5.3	D	subsoil	NA	2.91	NA	NA	NA	BPCA	30 to 100	2	17.88
	51.75	36.15	0-500	agriculture	573	5.3	D	topsoil	NA	5.6	NA	NA	NA	BPCA	30 to 100	2	10.5
	54	37.5	0-500	agriculture	715	4.1	D	subsoil	NA	0.32	NA	NA	NA	BPCA	30 to 100	5	8.94
	54	37.5	0-500	agriculture	715	4.1	D	topsoil	NA	3.44	NA	NA	NA	BPCA	30 to 100	5	3.64
(Rodionow et	67.48	86.42	0-500	forest	510	-7.4	D	subsoil	1.1	12.8	28.4	4.8	NA	BPCA	1 to 30	NA	13.87
al., 2006)	67.48	86.42	0-500	forest	510	-7.4	D	topsoil	0.6	7.4	30.3	5.5	NA	BPCA	1 to 30	NA	4.72
	67.48	86.42	0-500	forest	510	-7.4	D	subsoil	1	5.3	27.6	4.4	NA	BPCA	1 to 30	NA	4.2
	67.48	86.42	0-500	forest	510	-7.4	D	topsoil	0.98	3	28	3.9	NA	BPCA	1 to 30	NA	1.66
	67.49	86.42	0-500	forest	510	-7.4	D	topsoil	0.92	3.6	24	5.5	NA	BPCA	1 to 30	NA	4.04
	67.49	86.42	0-500	forest	510	-7.4	D	subsoil	1.58	0.8	18	4.8	NA	BPCA	1 to 30	NA	3.41
(Rodionov et	-38.75	-62.18	0-500	agriculture	582	15.6	C	topsoil	1.32	1.56	NA	5.8	NA	BPCA	30 to 100	2	7.12
al., 2010)	-38.38	-60.27	0-500	urban	731	14.5	C	topsoil	1.2	4.22	NA	5	NA	BPCA	30 to 100	2	10.08
	-38.38	-60.27	0-500	agriculture	731	14.5	C	topsoil	1.24	1.67	NA	5.5	NA	BPCA	30 to 100	2	9.18

	-38.37	-60.37	0-500	agriculture	731	14.5	C	topsoil	1.24	2.73	NA	5.3	NA	BPCA	30 to 100	2	7
	-37.77	-58.3	0-500	agriculture	843	13.8	C	topsoil	1.2	4.13	NA	5.4	NA	BPCA	30 to 100	3	18.09
	-37.77	-58.3	0-500	agriculture	843	13.8	C	topsoil	1.2	3.85	NA	4.7	NA	BPCA	30 to 100	2	12.58
	27.57	-98.9	0-500	grass	446	23.4	C	topsoil	1.77	1.51	NA	6.3	NA	BPCA	30 to 100	3	2.59
	31.17	-97.97	0-500	grass	829	20	C	topsoil	1.45	3.22	NA	6.1	NA	BPCA	30 to 100	2	10.4
	33.2	-100.22	500-1000	grass	507	17.7	B	topsoil	1.2	2.67	NA	5.8	NA	BPCA	30 to 100	3	7.36
	39.07	-95.6	0-500	grass	839	12.6	C	topsoil	1.24	4.03	NA	5.9	NA	BPCA	30 to 100	2	8.31
	44	-103.78	1500-2000	grass	497	6.8	D	topsoil	1.34	1.29	NA	5.5	NA	BPCA	30 to 100	4	12.3
	45.6	121.36	500-1000	agriculture	388	4.9	D	topsoil	1.34	2.04	NA	5.3	NA	BPCA	1 to 30	NA	7.37
	45.65	124.63	0-500	agriculture	423	4.5	D	topsoil	1.03	1.07	NA	5.3	NA	BPCA	30 to 100	4	11.13
	45.72	122.2	0-500	agriculture	378	4.9	D	topsoil	1.34	1.59	NA	4.9	NA	BPCA	30 to 100	3	4.26
	46.17	122.07	0-500	agriculture	410	4.2	D	topsoil	1.04	1.16	NA	5	NA	BPCA	<1	NA	12.03
	46.22	126.38	0-500	agriculture	545	3.6	D	topsoil	1.05	2.47	NA	5.2	NA	BPCA	<1	NA	19.2
	46.27	-106.23	500-1000	grass	274	6.5	B	topsoil	1.34	1.32	NA	5.9	NA	BPCA	>100	4	3.58
(Roth et al.,	50.92	6.35	0-500	agriculture	693	9.8	C	subsoil	NA	1	12	NA	NA	other	<1	NA	27.88
2012)	50.92	6.35	0-500	agriculture	693	9.8	C	subsoil	NA	1	12	NA	NA	BPCA	<1	NA	10.6
	50.92	6.35	0-500	agriculture	693	9.8	C	subsoil	NA	1	12	NA	NA	CTO 375	<1	NA	10.23
	50.92	6.35	0-500	agriculture	693	9.8	C	subsoil	NA	1	12	NA	NA	CTO 375	<1	NA	6.7
	50.93	6.95	0-500	agriculture	796	10	C	subsoil	NA	0.7	8	NA	NA	other	<1	NA	35.69
	50.93	6.95	0-500	agriculture	796	10	C	subsoil	NA	0.7	8	NA	NA	BPCA	<1	NA	16.35
	50.93	6.95	0-500	agriculture	796	10	C	subsoil	NA	0.7	8	NA	NA	CTO 375	<1	NA	15.62
	50.93	6.95	0-500	agriculture	796	10	C	subsoil	NA	0.7	8	NA	NA	CTO 375	<1	NA	6.7
	51	8	0-500	agriculture	750	10	C	subsoil	NA	1.4	22	NA	NA	CTO 375	30 to 100	NA	36.99

	51	8	0-500	NA	750	10	C	subsoil	NA	2.1	11	NA	NA	other	30 to 100	NA	21.56
	51	8	0-500	agriculture	750	10	C	subsoil	NA	1.4	22	NA	NA	other	30 to 100	NA	23.24
	51	8	0-500	NA	750	10	C	subsoil	NA	2.1	11	NA	NA	CTO 375	<1	NA	14.87
	51	8	0-500	agriculture	750	10	C	subsoil	NA	1.4	22	NA	NA	CTO 375	30 to 100	NA	16.35
	51	8	0-500	agriculture	750	10	C	subsoil	NA	1.4	22	NA	NA	BPCA	30 to 100	NA	7.8
	51	8	0-500	NA	750	10	C	subsoil	NA	2.1	11	7.5	NA	BPCA	30 to 100	NA	4.46
	51	8	0-500	NA	750	10	C	subsoil	NA	2.1	11	NA	NA	CTO 375	30 to 100	NA	3.16
(Rovira et al.,	38.8	0.2	0-500	NA	825	17.4	C	topsoil	NA	3.07	NA	5.6	NA	Cr2O6	30 to 100	NA	23.18
2009)	38.8	0.2	0-500	shrubs	825	17.4	C	topsoil	NA	2.89	NA	5.5	medium	Cr2O6	30 to 100	NA	18.6
	38.8	0.2	0-500	NA	825	17.4	C	topsoil	NA	3.73	NA	NA	medium	Cr2O6	30 to 100	NA	18.71
	38.8	0.2	0-500	shrubs	825	17.4	C	topsoil	NA	2.5	NA	5.5	high	Cr2O6	30 to 100	NA	18.79
	38.8	0.2	0-500	NA	825	17.4	C	topsoil	NA	4.62	NA	NA	NA	Cr2O6	30 to 100	NA	20.67
	38.8	0.2	0-500	NA	825	17.4	C	topsoil	NA	3.74	NA	NA	high	Cr2O6	30 to 100	NA	20.67
	38.8	0.2	0-500	NA	825	17.4	C	topsoil	NA	2.44	NA	NA	medium	Cr2O6	30 to 100	NA	20.96
	38.8	0.2	0-500	shrubs	825	17.4	C	topsoil	NA	5.4	NA	5.7	NA	Cr2O6	30 to 100	NA	21.07
(Rumpel et al.,	19.88	102.33	500-1000	agriculture	1403	25	C	topsoil	NA	1.79	NA	5.4	NA	Cr2O6	30 to 100	2	17.23
2006)	19.88	102.33	500-1000	agriculture	1403	25	C	topsoil	NA	2.65	NA	5.8	NA	Cr2O6	30 to 100	2	16.05
	19.88	102.33	500-1000	agriculture	1403	25	C	topsoil	NA	1.49	NA	5.3	NA	Cr2O6	30 to 100	2	16.05
	19.88	102.33	500-1000	agriculture	1403	25	C	topsoil	NA	2.04	NA	5.4	NA	Cr2O6	30 to 100	2	13.92
	19.88	102.33	500-1000	agriculture	1403	25	C	topsoil	NA	1.21	NA	5.7	NA	Cr2O6	30 to 100	2	12.98
	19.88	102.33	500-1000	agriculture	1403	25	C	topsoil	NA	1.71	NA	5.2	NA	Cr2O6	30 to 100	2	12.98
	19.88	102.33	500-1000	agriculture	1403	25	C	subsoil	NA	1.16	NA	5.1	NA	Cr2O6	30 to 100	2	10.86
	19.88	102.33	500-1000	agriculture	1403	25	C	subsoil	NA	1.59	NA	5.4	NA	Cr2O6	30 to 100	2	10.62
	19.88	102.33	500-1000	agriculture	1403	25	C	subsoil	NA	0.75	NA	5.1	NA	Cr2O6	30 to 100	2	9.91

	19.88	102.33	500-1000	agriculture	1403	25	C	subsoil	NA	5	NA	5.5	NA	Cr2O6	30 to 100	2	9.68
	19.88	102.33	500-1000	agriculture	1403	25	C	subsoil	NA	0.44	NA	5.3	NA	Cr2O6	30 to 100	2	9.44
	19.88	102.33	500-1000	agriculture	1403	25	C	subsoil	NA	8.1	NA	5	NA	Cr2O6	30 to 100	2	8.73
	19.88	102.33	500-1000	agriculture	1403	25	C	subsoil	NA	1.18	NA	5.2	NA	Cr2O6	30 to 100	2	8.26
	19.88	102.33	500-1000	agriculture	1403	25	C	subsoil	NA	0.75	NA	4.8	NA	Cr2O6	30 to 100	2	8.02
	19.88	102.33	500-1000	agriculture	1403	25	C	subsoil	NA	0.76	NA	5.1	NA	Cr2O6	30 to 100	2	6.84
(Schmid et al.,	48.97	9.27	0-500	agriculture	NA	NA	C	subsoil	NA	4.1	NA	6.8	NA	UV Oxidation	<1	NA	37.07
2002)	48.97	9.27	0-500	agriculture	NA	NA	C	subsoil	NA	1.04	NA	6.5	NA	UV Oxidation	<1	NA	35.58
	48.97	9.27	0-500	agriculture	NA	NA	C	subsoil	NA	0.95	NA	NA	NA	UV Oxidation	<1	NA	33.68
	48.97	9.27	0-500	agriculture	NA	NA	C	subsoil	NA	1.03	NA	NA	NA	UV Oxidation	<1	NA	21.36
	48.97	9.27	0-500	agriculture	NA	NA	C	subsoil	NA	0.37	NA	6.8	NA	UV Oxidation	<1	NA	16.22
	48.97	9.27	0-500	agriculture	NA	NA	C	subsoil	NA	1.02	NA	6.7	NA	UV Oxidation	<1	NA	14.71
	48.97	9.27	0-500	agriculture	NA	NA	C	subsoil	NA	0.23	NA	6.7	NA	UV Oxidation	<1	NA	13.04
	48.97	9.27	0-500	agriculture	NA	NA	C	subsoil	NA	1.48	NA	6.8	NA	UV Oxidation	<1	NA	7.43
	48.97	9.27	0-500	agriculture	NA	NA	C	subsoil	NA	0.49	NA	NA	NA	UV Oxidation	<1	NA	4.08
	48.97	9.27	0-500	agriculture	NA	NA	C	subsoil	NA	0.61	NA	NA	NA	UV Oxidation	<1	NA	1.64
(Schmidt et al.,	48.42	11.57	0-500	forest	1400	NA	C	subsoil	NA	2.79	30.3	5.8	NA	UV Oxidation	<1	NA	30
1999)	48.42	11.57	0-500	forest	1400	NA	C	subsoil	NA	3.74	25.7	7.6	NA	UV Oxidation	<1	NA	15
	51.97	5.67	0-500	agriculture	800	NA	C	topsoil	NA	1.75	3.3	7.6	NA	UV Oxidation	<1	NA	2
	52.15	9.95	0-500	grass	630	NA	C	subsoil	NA	1.78	23.9	6.9	NA	UV Oxidation	<1	NA	45
	52.15	9.95	0-500	grass	630	NA	C	subsoil	NA	1.19	17.6	6.1	NA	UV Oxidation	<1	NA	23
	52.15	9.95	0-500	grass	630	NA	C	topsoil	NA	2.36	21.7	6.9	NA	UV Oxidation	<1	NA	19
	52.15	9.95	0-500	grass	630	NA	C	topsoil	NA	1.83	16.8	5.9	NA	UV Oxidation	<1	NA	14
	52.27	10.52	0-500	grass	630	NA	C	subsoil	NA	1.28	18.7	7.4	NA	UV Oxidation	<1	NA	3

	52.27	10.52	0-500	grass	630	NA	C	subsoil	NA	1.33	22.1	7.6	NA	UV Oxidation	<1	NA	3
	52.27	10.52	0-500	grass	630	NA	C	topsoil	NA	1.35	18	7.2	NA	UV Oxidation	NA	NA	2
	52.27	10.52	0-500	NA	630	NA	C	NA	NA	1.9	NA	7.2	NA	CTO 375	<1	NA	15.8
	52.88	11.03	0-500	agriculture	480	NA	C	subsoil	NA	2.26	19.2	7	NA	UV Oxidation	NA	NA	15
	52.88	11.03	0-500	agriculture	480	NA	C	topsoil	NA	2.37	19.3	4	NA	UV Oxidation	<1	NA	9
	54.3	11.01	0-500	forest	480	NA	C	topsoil	NA	1.51	15.7	6.5	NA	UV Oxidation	<1	NA	2
	54.47	11.13	0-500	grass	570	NA	C	topsoil	NA	1.57	8.3	5.4	NA	UV Oxidation	<1	NA	4
	54.47	11.13	0-500	grass	570	NA	C	subsoil	NA	0.48	17.7	4.1	NA	UV Oxidation	NA	NA	8
	54.47	11.13	0-500	grass	570	NA	C	subsoil	NA	1.2	11.4	3.7	NA	UV Oxidation	<1	NA	15
(Schmidt et al.,	47.85	11.6	500-1000	forest	NA	NA	C	subsoil	NA	2.79	NA	6.4	NA	UV Oxidation	<1	NA	30
2002)	51.55	12	0-500	agriculture	NA	NA	C	subsoil	NA	2.26	NA	5.9	NA	UV Oxidation	30 to 100	3	15
	52.2	9.95	0-500	grass	NA	NA	C	subsoil	NA	1.28	NA	NA	NA	UV Oxidation	<1	NA	3
	52.2	9.9	0-500	grass	NA	NA	C	subsoil	NA	1.78	NA	NA	NA	UV Oxidation	<1	NA	45
	52.2	9.85	0-500	grass	NA	NA	C	subsoil	NA	1.19	NA	6	NA	UV Oxidation	30 to 100	3	23
	54.4	11.15	0-500	grass	NA	NA	C	subsoil	NA	1.2	NA	6.1	NA	UV Oxidation	NA	NA	15
(Schulze et al.,																	
1999)	60.74	89.15	0-500	forest	663	-3.3	D	complete	NA	NA	NA	3.9	medium	other	30 to 100	3	1.87
(Shindo et al.,	31.72	131.07	0-500	agriculture	NA	NA	C	subsoil	NA	8.8	NA	NA	NA	physical	<1	NA	10.28
2004)	31.72	131.07	0-500	grass	NA	NA	C	subsoil	NA	8.38	NA	NA	NA	physical	<1	NA	7.86
	31.72	131.07	0-500	grass	NA	NA	C	subsoil	NA	9.56	NA	NA	NA	physical	<1	NA	5.43
	31.99	130.95	0-500	agriculture	NA	NA	C	subsoil	NA	7.83	NA	NA	NA	physical	30 to 100	NA	21.2
	32.72	130.67	0-500	grass	NA	NA	C	subsoil	NA	9.26	NA	NA	NA	physical	1 to 30	NA	15.55
	34.72	137.85	0-500	forest	NA	NA	C	subsoil	NA	4.74	NA	NA	NA	physical	<1	NA	3.38
	34.8	132.85	0-500	forest	NA	NA	C	subsoil	NA	5.82	NA	NA	NA	physical	<1	NA	6.17

	35.22	138.62	0-500	forest	NA	NA	C	subsoil	NA	18.1	NA	NA	NA	physical	>100	NA	19.61
	35.22	138.62	0-500	forest	NA	NA	C	subsoil	NA	8.47	NA	NA	NA	physical	>100	NA	4.13
	35.22	138.62	0-500	forest	NA	NA	C	subsoil	NA	11.8	NA	NA	NA	physical	<1	NA	3.8
	35.22	132.67	0-500	grass	NA	NA	C	subsoil	NA	14.6	NA	NA	NA	physical	<1	NA	32.74
	35.45	133.77	0-500	forest	NA	NA	C	subsoil	NA	12.5	NA	NA	NA	physical	30 to 100	NA	7.3
	35.55	134.82	0-500	forest	NA	NA	C	subsoil	NA	4.7	NA	NA	NA	physical	<1	NA	5.47
	35.55	134.82	0-500	forest	NA	NA	C	subsoil	NA	12.6	NA	NA	NA	physical	<1	NA	20
	36.03	140.07	0-500	grass	NA	NA	C	subsoil	NA	3.19	NA	NA	NA	physical	<1	NA	7.3
	36.38	139.73	0-500	forest	NA	NA	C	subsoil	NA	12.7	NA	NA	NA	physical	30 to 100	NA	7.65
	36.57	139.75	0-500	agriculture	NA	NA	C	subsoil	NA	5.61	NA	NA	NA	physical	<1	NA	7.27
	39.2	141.12	0-500	forest	NA	NA	C	subsoil	NA	11.2	NA	NA	NA	physical	<1	NA	26.16
	39.2	141.12	0-500	forest	NA	NA	C	subsoil	NA	11.5	NA	NA	NA	physical	<1	NA	21.39
	39.68	140.98	0-500	grass	NA	NA	C	subsoil	NA	7.83	NA	NA	NA	physical	<1	NA	11.58
	39.73	141.08	0-500	grass	NA	NA	C	subsoil	NA	3.94	NA	NA	NA	physical	<1	NA	6.37
	42.07	143.15	0-500	grass	NA	NA	C	subsoil	NA	12.5	NA	NA	NA	physical	1 to 30	NA	15.84
	42.07	143.15	0-500	grass	NA	NA	C	subsoil	NA	12.1	NA	NA	NA	physical	1 to 30	NA	9.17
	42.98	141.57	0-500	forest	NA	NA	C	subsoil	NA	7	NA	NA	NA	physical	1 to 30	NA	9.34
(Simpson and	-27.57	151.95	500-1000	grass	955	15	C	topsoil	NA	2.7	50	7.4	NA	UV Oxidation	30 to 100	2	10.74
Hatcher, 2004)	28	-82	0-500	peat	1220	22	C	NA	NA	55.2	NA	7.6	NA	CTO 375	NA	NA	0.63
	52.27	10.52	0-500	grass	630	NA	C	topsoil	NA	0.5	18	5.9	NA	UV Oxidation	1 to 30	NA	5
	53.53	-113.5	500-1000	NA	480	4	D	NA	NA	5.2	NA	7.6	NA	CTO 375	NA	NA	22.3
(Skjemstad et	-19.6	147.4	0-500	agriculture	1100	25	A	topsoil	1.3	2.25	28	5.6	NA	UV Oxidation	30 to 100	2	6.22
al., 1999)	-19.6	147.4	0-500	agriculture	1100	25	A	topsoil	1.3	2.36	33	5.2	NA	UV Oxidation	<1	2	5.08
	-18.65	146.15	0-500	agriculture	2061	25	A	topsoil	1.3	1.75	18	5.1	NA	UV Oxidation	30 to 100	2	42.86

	-18.65	146.15	0-500	shrubs	2061	25	A	topsoil	1.3	2.41	10	6.6	NA	UV Oxidation	30 to 100	5	21.16
	-18.65	146.15	0-500	grass	2061	25	A	topsoil	1.3	1.42	23	8	NA	UV Oxidation	30 to 100	2	9.15
	-18.65	146.15	0-500	agriculture	2061	25	A	topsoil	1.3	1.05	22	5.9	NA	UV Oxidation	30 to 100	2	7.62
(Skjemstad et	-27.57	151.95	500-1000	agriculture	955	15	C	topsoil	NA	1.25	78	4.7	NA	UV Oxidation	30 to 100	2	51.2
al., 2001)	-27.57	151.95	500-1000	agriculture	955	15	C	topsoil	NA	1.14	80	4.3	NA	UV Oxidation	30 to 100	2	50.88
	-27.57	151.95	500-1000	agriculture	955	15	C	topsoil	NA	1.21	78	4.3	NA	UV Oxidation	30 to 100	2	48.76
	-27.57	151.95	500-1000	grass	955	15	C	topsoil	NA	1.82	69	4.3	NA	UV Oxidation	30 to 100	2	28.02
	-27.57	151.95	500-1000	agriculture	955	15	C	topsoil	NA	0.75	52	NA	NA	UV Oxidation	30 to 100	2	26.67
	-27.57	151.95	500-1000	agriculture	955	15	C	topsoil	NA	0.94	50	NA	NA	UV Oxidation	30 to 100	2	21.28
	-27.57	151.95	500-1000	agriculture	955	15	C	topsoil	NA	1.19	53	NA	NA	UV Oxidation	30 to 100	2	24.37
	-27.57	151.95	500-1000	NA	955	NA	C	NA	NA	3.5	NA	4.3	NA	CTO 375	NA	NA	17.4
(Skjemstad et	31.08	-97.36	0-500	agriculture	937	19	C	topsoil	NA	3.69	50	6.8	NA	UV Oxidation	1 to 30	2	20.6
al., 2002)	41.53	-88.12	0-500	agriculture	121	10	D	topsoil	NA	2.87	40	5.7	NA	UV Oxidation	<1	NA	23
	45.72	-94.08	0-500	agriculture	NA	NA	C	topsoil	NA	4.13	32	7.4	NA	UV Oxidation	1 to 30	NA	32.93
	45.72	-118	1500-2000	agriculture	321	11	B	topsoil	NA	1.03	13	6.2	NA	UV Oxidation	30 to 100	3	34.95
	45.76	-93.07	0-500	agriculture	NA	NA	D	topsoil	NA	1.86	10	5.6	NA	UV Oxidation	30 to 100	NA	9.68
(Song et al., 2002)	23.13	113.27	0-500	agriculture	1982	22	C	topsoil	NA	1.55	NA	NA	NA	NMR	1 to 30	2	35.9
(Soucémariana	49.07	-74.35	0-500	forest	950	-0.5	D	complete	NA	NA	5	NA	low	other	1 to 30	4	4.31
din et al., 2014)	49.28	-73.9	0-500	forest	950	-0.5	D	complete	NA	NA	5	NA	low	other	>100	4	2.07
	49.32	-73.89	0-500	forest	950	-0.5	D	complete	NA	NA	5	NA	low	other	>100	4	2.04
	50.3	-72.07	0-500	forest	950	-0.5	D	complete	NA	NA	5	NA	low	other	>100	4	1.79
	50.32	-72.05	500-1000	forest	950	-0.5	D	complete	NA	NA	5	NA	low	other	>100	4	1.01

	50.33	-73.92	0-500	forest	950	-1.25	D	complete	NA	NA	5	8.4	low	other	NA	NA	2.2
	50.35	-73.7	0-500	forest	950	-1.25	D	complete	NA	NA	5	8	low	other	NA	NA	2.03
	50.35	-73.7	0-500	forest	950	-1.25	D	complete	NA	NA	5	8.2	low	other	NA	NA	1.2
	50.39	-73.96	0-500	forest	950	-1.25	D	complete	NA	NA	5	8	low	other	NA	NA	4.01
	50.47	-76.57	0-500	forest	825	-1.25	D	complete	NA	NA	8	4.3	low	other	>100	4	2.86
	50.48	-76.55	0-500	forest	825	-1.25	D	complete	NA	NA	8	4.2	low	other	>100	4	1.92
	50.5	-76.35	0-500	forest	825	-1.25	D	complete	NA	NA	8	4.2	low	other	30 to 100	4	1.24
	50.52	-76.34	0-500	forest	825	-1.25	D	complete	NA	NA	8	4.2	low	other	30 to 100	4	1.71
	50.56	-68.83	0-500	forest	1100	-1.25	D	complete	NA	NA	5	NA	low	other	>100	4	0.6
	50.58	-68.77	0-500	forest	1100	-1.25	D	complete	NA	NA	5	NA	low	other	>100	4	3.39
	50.6	-74.77	0-500	forest	830	-1.75	D	complete	NA	NA	4	7.1	low	other	30 to 100	4	1.62
	50.6	-74.78	0-500	forest	830	-1.75	D	complete	NA	NA	4	7.8	low	other	30 to 100	4	1.09
	50.7	-74.78	0-500	forest	830	-1.75	D	complete	NA	NA	4	8.2	low	other	30 to 100	4	4.76
	50.83	-68.98	0-500	forest	1100	-1.25	D	complete	NA	NA	5	NA	low	other	>100	4	3.93
	50.83	-68.99	0-500	forest	1100	-1.25	D	complete	NA	NA	5	NA	low	other	<1	4	1.34
	50.97	-74.57	0-500	forest	950	-1.25	D	complete	NA	NA	5	4.2	low	other	30 to 100	4	2.33
	50.97	-75.22	0-500	forest	830	-1.75	D	complete	NA	NA	4	4.2	low	other	>100	4	1.41
	50.98	-75.22	0-500	forest	830	-1.75	D	complete	NA	NA	4	8.2	low	other	30 to 100	4	1.6
(Van den	38.6	-121.5	0-500	NA	NA	NA	C	topsoil	NA	0.33	NA	6.3	NA	other	30 to 100	3	27.52
Heuvel et al.,	39.75	-75.55	0-500	NA	NA	NA	C	topsoil	NA	1.35	NA	5.9	NA	other	1 to 30	2	8.41
2005)	41.4	-72.9	0-500	NA	NA	NA	C	topsoil	NA	1.36	NA	5.4	NA	other	1 to 30	2	16.69
	42.3	-83.75	0-500	NA	NA	NA	D	topsoil	NA	0.23	NA	6.8	NA	other	<1	NA	39.48
	46	9	0-500	NA	NA	NA	C	topsoil	NA	1.57	NA	NA	NA	other	30 to 100	NA	44.82
	46	9	0-500	NA	NA	NA	C	topsoil	NA	1.48	NA	NA	NA	other	30 to 100	NA	10.74

	53.5	-2	0-500	NA	NA	NA	C	topsoil	NA	1.8	NA	NA	NA	other	>100	NA	29.01
	55.97	8.65	0-500	NA	NA	NA	C	topsoil	NA	1.48	NA	NA	NA	other	30 to 100	NA	44.48
(Wiedemeier et	-36.52	149.5	0-500	peat	1000	15	C	subsoil	NA	20.09	NA	NA	NA	BPCA	30 to 100	3	21
al., 2013)	-36.52	149.5	0-500	peat	1000	15	C	subsoil	NA	6.38	NA	NA	NA	BPCA	30 to 100	3	14.3
	-36.52	149.5	0-500	peat	1000	15	C	topsoil	NA	27.12	NA	NA	NA	BPCA	30 to 100	3	13.54
	-36.52	149.5	0-500	peat	1000	15	C	subsoil	NA	35.47	NA	NA	NA	BPCA	30 to 100	3	12.27
(Yang et al.,	32.75	-97.32	0-500	urban	880	18.6	C	topsoil	NA	2.8	NA	4.3	NA	Cr2O6	>100	NA	1.34
2010)	32.75	-97.32	0-500	urban	880	18.6	C	topsoil	NA	4	NA	NA	NA	Cr2O6	<1	NA	0.76
	32.75	-97.32	0-500	urban	880	18.6	C	topsoil	NA	2.8	NA	4.3	NA	CTO 375	<1	NA	0.44
	32.75	-97.32	0-500	urban	880	18.6	C	topsoil	NA	4	NA	NA	NA	CTO 375	30 to 100	NA	0.29
(Zhan et al.,	34.34	107.93	500-1000	grass	600	13.3	C	subsoil	1.2	0.45	NA	NA	NA	other	1 to 30	2	16.62
2013)	34.34	107.93	500-1000	grass	600	13.3	C	topsoil	1.21	0.65	NA	NA	NA	other	1 to 30	2	8.62
	34.34	107.93	500-1000	grass	600	13.3	C	subsoil	1.2	0.6	NA	NA	NA	other	1 to 30	2	7.94
	34.74	105	1000-1500	grass	490	11	B	subsoil	1.25	0.14	NA	NA	NA	other	<1	NA	19.44
	34.74	105	1000-1500	grass	490	11	B	subsoil	1.25	0.32	NA	NA	NA	other	<1	NA	10.15
	34.74	105	1000-1500	grass	490	11	B	topsoil	1.37	0.63	NA	NA	NA	other	<1	NA	6.88
	34.98	106.24	1500-2000	grass	490	12	B	topsoil	1.15	0.74	NA	NA	NA	other	<1	NA	13.7
	34.98	106.24	1500-2000	grass	490	12	B	subsoil	1.11	0.67	NA	NA	NA	other	<1	NA	9.04
	34.98	106.24	1500-	grass	490	12	B	subsoil	1.11	0.77	NA	NA	NA	other	<1	NA	6.33

		2000														
35.21	110.12	500-1000	grass	529	14.4	B	subsoil	1.47	0.06	NA	NA	NA	other	1 to 30	2	21.79
35.21	110.12	500-1000	grass	529	14.4	B	topsoil	1.15	0.24	NA	NA	NA	other	1 to 30	2	20.64
35.21	110.12	500-1000	grass	529	14.4	B	subsoil	1.22	0.17	NA	NA	NA	other	1 to 30	2	18.57
		1500-														
35.48	104.69	2000	grass	450	8	D	subsoil	1.1	0.65	NA	NA	NA	other	<1	NA	5.98
		1500-														
35.48	104.69	2000	grass	450	8	D	topsoil	1.16	0.81	NA	NA	NA	other	30 to 100	NA	5.08
		1500-														
35.48	104.69	2000	grass	450	8	D	subsoil	1.04	0.81	NA	NA	NA	other	<1	NA	3.33
		1000-														
35.68	106.24	1500	grass	480	9	D	topsoil	1.17	1.37	NA	NA	NA	other	<1	NA	5.69
		1000-														
35.68	106.24	1500	grass	480	9	D	subsoil	1.13	1.09	NA	NA	NA	other	30 to 100	NA	3.98
		1000-														
35.68	106.24	1500	grass	480	9	D	subsoil	1.1	0.98	NA	NA	NA	other	<1	NA	3.17
35.71	103.43	>2000	grass	350	7	B	subsoil	1.15	0.26	NA	NA	NA	other	<1	NA	20.61
35.71	103.43	>2000	grass	350	7	B	subsoil	1.23	0.35	NA	NA	NA	other	<1	NA	18.78
35.71	103.43	>2000	grass	350	7	B	topsoil	1.36	0.41	NA	NA	NA	other	<1	NA	14.03
		1000-														
35.95	107.93	1500	grass	570	8.5	D	subsoil	1.26	0.24	NA	NA	NA	other	<1	NA	14.4
		1000-														
35.95	107.93	1500	grass	570	8.5	D	subsoil	1.29	0.32	NA	NA	NA	other	<1	NA	10.26
35.95	107.93	1000-	grass	570	8.5	D	topsoil	1.31	0.69	NA	NA	NA	other	<1	NA	8.55

		1500													
		1500-													
36.24	103.05	2000	grass	315	9.8	B	topsoil	1.29	0.32	NA	NA	NA	other	<1	NA	32.85
		1500-													
36.24	103.05	2000	grass	315	9.8	B	subsoil	1.24	0.13	NA	NA	NA	other	<1	NA	27.1
		1500-													
36.24	103.05	2000	grass	315	9.8	B	subsoil	1.15	0.19	NA	NA	NA	other	<1	NA	15.42
		1000-													
36.56	104.68	1500	grass	200	10	B	topsoil	1.11	0.36	NA	NA	NA	other	<1	NA	14.25
		1000-													
36.56	104.68	1500	grass	200	10	B	subsoil	1.26	0.33	NA	NA	NA	other	1 to 30	NA	14.22
		1000-													
36.56	104.68	1500	grass	200	10	B	subsoil	1.26	0.27	NA	NA	NA	other	<1	NA	8.53
		1000-													
36.66	109.19	1500	grass	510	10.3	D	subsoil	1.29	0.12	NA	NA	NA	other	1 to 30	NA	12.03
		1000-													
36.66	109.19	1500	grass	510	10.3	D	subsoil	1.3	0.25	NA	NA	NA	other	<1	NA	9.12
		1000-													
36.66	109.19	1500	grass	510	10.3	D	topsoil	1.31	0.33	NA	NA	NA	other	<1	NA	6.57
		1000-													
36.67	106.1	1500	grass	435	7	D	subsoil	1.29	0.21	NA	NA	NA	other	<1	NA	21.48
		1000-													
36.67	106.1	1500	grass	435	7	D	topsoil	1.26	0.17	NA	NA	NA	other	<1	NA	13.7
36.67	106.1	1000-	grass	435	7	D	subsoil	1.3	0.19	NA	NA	NA	other	<1	NA	12.73

		1500														
		1000-														
36.9	111.16	1500	grass	470	12.6	B	subsoil	1.38	0.32	NA	NA	NA	other	1 to 30	NA	9.99
		1000-														
36.9	111.16	1500	grass	470	12.6	B	subsoil	1.37	0.45	NA	3.9	NA	other	1 to 30	NA	8.59
		1000-														
36.9	111.16	1500	grass	470	12.6	B	topsoil	1.37	0.99	NA	3.9	NA	other	1 to 30	NA	5.17
		1500-														
37.19	106.77	2000	grass	510	10	D	subsoil	1.42	0.11	NA	NA	NA	other	<1	NA	13.14
		1500-														
37.19	106.77	2000	grass	510	10	D	subsoil	1.34	0.2	NA	NA	NA	other	<1	NA	7.49
		1500-														
37.19	106.77	2000	grass	510	10	D	topsoil	1.26	0.24	NA	NA	NA	other	<1	NA	6.93
		1000-														
37.51	108.45	1500	grass	450	8.8	B	subsoil	1.42	0.09	NA	NA	NA	other	<1	NA	15.27
		1000-														
37.51	108.45	1500	grass	450	8.8	B	subsoil	1.49	0.1	NA	NA	NA	other	<1	NA	14.77
		1000-														
37.51	108.45	1500	grass	450	8.8	B	topsoil	1.44	0.1	NA	NA	NA	other	<1	NA	24.83
		1000-														
37.99	111.09	1500	grass	460	9.1	D	subsoil	1.26	0.19	NA	3.9	NA	other	30 to 100	3	15.55
		1000-														
37.99	111.09	1500	grass	460	9.1	D	subsoil	1.32	0.14	NA	NA	NA	other	1 to 30	3	17.74
	37.99	111.09	1000-	grass	460	9.1	D	topsoil	1.23	0.36	NA	NA	NA	other	1 to 30	3	11.04

		1500														
		1000-														
38.13	108.45	1500	grass	450	8.8	B	subsoil	1.71	0.04	NA	NA	NA	other	<1	NA	22.45
		1000-														
38.13	108.45	1500	grass	450	8.8	B	subsoil	1.77	0.05	NA	NA	NA	other	<1	NA	18.95
		1000-														
38.13	108.45	1500	grass	450	8.8	B	topsoil	1.69	0.05	NA	NA	NA	other	>100	NA	17.98
39.11	111.15	500-1000	grass	400	7	B	subsoil	1.52	0.05	NA	NA	NA	other	<1	NA	31.17
39.11	111.15	500-1000	grass	400	7	B	subsoil	1.52	0.05	NA	NA	NA	other	<1	NA	30.77
39.11	111.15	500-1000	grass	400	7	B	topsoil	1.42	0.15	NA	NA	NA	other	<1	NA	10.95

References:

Aciego Pietri, J. C., and Brookes, P. C. (2008). Relationships between soil pH and microbial properties in a UK arable soil. *Soil Biol. Biochem.* 40, 1856–1861. doi: 10.1016/j.soilbio.2008.03.020

Archibald, S., Lehmann, C. E. R., Gómez-Dans, J. L., and Bradstock, R. A. (2013). Defining pyromes and global syndromes of fire regimes. *Proc. Natl. Acad. Sci. U.S.A.* 110, 6442–6447. doi: 10.1073/pnas.1211466110

Ascough, P. L., Bird, M. I., Francis, S. M., Thornton, B., Midwood, A. J., Scott, A. C., et al. (2011). Variability in oxidative degradation of charcoal: influence of production conditions and environmental exposure. *Geochim. Cosmochim. Acta* 75, 2361–2378. doi: 10.1016/j.gca.2011.02.002

Biederman, L. A., and Harpole, W. S. (2013). Biochar and its effects on plant productivity and nutrient cycling: a meta-analysis. *GCB Bioenergy* 5, 202–214. doi: 10.1111/gcbb.12037

Bird, M. (2014). "Test procedures for biochar analysis in soils," in *Biochar for Environmental Management - Science, Technology and Implementation*, eds J. Lehmann and S. Joseph (London: Routledge), 677–714.

Bird, M. I., Moyo, C., Veenendaal, E. M., Lloyd, J., and Frost, P. (1999). Stability of elemental carbon in a savanna soil. *Geoderma*13, 923–932. doi: 10.1029/1999gb900067

Bird, M. I., Wynn, J. G., Saiz, G., Wurster, C. M., and McBeath, A. (2015). The pyrogenic carbon cycle. *Annu. Rev. Earth Planet. Sci.* 43, 273–298. doi: 10.1146/annurev-earth-060614-105038

Bowman, D. M. J. S., Murphy, B. P., Williamson, G. J., and Cochrane, M. A. (2014). Pyrogeographic models, feedbacks and the future of global fire regimes. *Glob. Ecol. Biogeogr.* 23, 821–824. doi: 10.1111/geb.12180

Braadbaart, F., Poole, I., and van Brussel, A. A. (2009). Preservation potential of charcoal in alkaline environments: an experimental approach and implications for the archaeological record. *J. Archaeol. Sci.* 36, 1672–1679. doi: 10.1016/j.jas.2009.03.006

Bucheli, T. D., Blum, F., Desaules, A., and Gustafsson, O. (2004). Polycyclic aromatic hydrocarbons, black carbon, and molecular markers in soils of Switzerland. *Chemosphere* 56, 1061–1076. doi: 10.1016/j.chemosphere.2004.06.002

Caria, G., Arrouays, D., Dubromel, E., Jolivet, C., Ratié, C., Bernoux, M., et al. (2011). Black carbon estimation in French calcareous soils using chemo-thermal oxidation method. *Soil Use Manag.* 27, 333–339. doi: 10.1111/j.1475-2743.2011.00349.x

Crane-Droesch, A., Abiven, S., Jeffery, S., and Torn, M. S. (2013). Heterogeneous global crop yield response to biochar: a meta-regression analysis. *Environ. Res. Lett.* 8:044049. doi: 10.1088/1748-9326/8/4/044049

Czimczik, C. I., Preston, C. M., Schmidt, M. W. I., and Schulze, E.-D. (2003). How surface fire in Siberian Scots pine forests affects soil organic carbon in the forest floor: stocks, molecular structure, and conversion to black carbon (charcoal). *Global Biogeochem. Cycles* 17, 1–14. doi: 10.1029/2002GB001956

Danielson, J. J., and Gesch, D. B. (2011). *Global Multi-Resolution Terrain Elevation Data 2010 (GMTED2010)*. U.S. Geological Survey Open-File Report 2011–1073, 26.

DeLaune, R. D., Patrick, J. W. H., and Casselman, M. E. (1981). Effect of sediment pH and redox conditions on degradation of benzo(a)pyrene. *Mar. Pollut. Bull.* 12, 251–253. doi: 10.1016/0025-326X(81)90366-0

Dinel, H., Schnitzer, M., and Meyhuys, G. R. (1990). "Soil lipids: origin, nature, content, decomposition, and effect on soil physical properties," in *Soil Biochemistry*, 6th Edn., eds J. M. Bollag and G. Stotzky (New York, NY: Marcel Dekker Inc.), 397–429.

Dwyer, E., Pinnock, S., Gregoire, J.-M., and Pereira, J. M. C. (2000). Global spatial and temporal distribution of vegetation fire as determined from satellite observations. *Int. J. Remote Sens.* 21, 1289–1302. doi: 10.1080/014311600210182

Eckmeier, E., Rosch, M., Ehrmann, O., Schmidt, M. W. I., Schier, W., and Gerlach, R. (2007). Conversion of biomass to charcoal and the carbon mass balance from a slash-and-burn experiment in a temperate deciduous forest. *Holocene* 17, 539–542. doi: 10.1177/0959683607077041

ESRI (2016). *ArcGIS Online*. Available online at: www.arcgis.com

FAO/IIASA/ISRIC/ISSCAS/JRC (2012). *Harmonized World Soil Database (Version 1.2)*. Rome; Laxenburg: FAO; IIASA.

Forbes, M. S., Raison, R. J., and Skjemstad, J. O. (2006). Formation, transformation and transport of black carbon (charcoal) in terrestrial and aquatic ecosystems. *Sci. Total Environ.* 370, 190–206. doi: 10.1016/j.scitotenv.2006.06.007

Friedl, M. A., Sulla-Menashe, D., Tan, B., Schneider, A., Ramankutty, N., Sibley, A., et al. (2010). MODIS Collection 5 global land cover: algorithm refinements and characterization of new datasets. *Remote Sens. Environ.* 114, 168–182. doi: 10.1016/j.rse.2009.08.016

Glaser, B., Haumaier, L., Guggenberger, G., and Zech, W. (1998). Black carbon in soils : the use of benzenecarboxylic acids as specific markers. *Org. Geochem.* 29, 811–819. doi: 10.1016/S0146-6380(98)00194-6

Gustafsson, O., Bucheli, D., Kukulska, Z., Andersson, M., Largeau, C., Rouzaud, J.-N., et al. (2001). Evaluation of a protocol for the quantification of black carbon in sediments. *Global Biogeochem. Cycles* 15, 881–890. doi: 10.1029/2000GB001380

Gustafsson, O., Haghseta, F., Chan, C., Macfarlane, J., and Gschwend, P. M. (1997). Quantification of the dilute sedimentary soot phase: implications for PAH speciation and bioavailability. *Environ. Sci. Technol.* 31, 203–209. doi: 10.1021/es960317s

Hammes, K., and Abiven, S. (2013). "Identification of black carbon in the earth system," in *Fire Phenomena and the Earth System*, ed C. M. Belcher (Chichester, UK: John Wiley & Sons), 157–176.

Hammes, K., Schmidt, M. W. I., Smernik, R. J., Currie, L. A., Ball, W. P., Nguyen, T. H., et al. (2007). Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere. *Global Biogeochem. Cycles* 21, 1–18. doi: 10.1029/2006GB002914

Hassink, J. (1997). The capacity of soils to preserve organic C and N by their association with clay and silt particles. *Plant Soil* 191, 77–87. doi: 10.1023/A:1004213929699

Kemmitt, S. J., Wright, D., Goulding, K. W. T., and Jones, D. L. (2006). pH regulation of carbon and nitrogen dynamics in two agricultural soils. *Soil Biol. Biochem.* 38, 898–911. doi: 10.1016/j.soilbio.2005.08.006

Knicker, H., Wiesmeier, M., and Dick, D. P. (2008). A simplified method for the quantification of pyrogenic organic matter in grassland soils via chemical oxidation. *Geoderma* 147, 69–74. doi: 10.1016/j.geoderma.2008.07.008

Kottek, M., Grieser, J., Beck, C., Rudolf, B., and Rubel, F. (2006). World map of the Köppen-Geiger climate classification updated. *Meteorol. Zeitschrift* 15, 259–263. doi: 10.1127/0941-2948/2006/0130

Lehmann, J., Skjemstad, J., Sohi, S., Carter, J., Barson, M., Falloon, P., et al. (2008). Australian climate–carbon cycle feedback reduced by soil black carbon. *Nat. Geosci.* 1, 832–835. doi: 10.1038/ngeo358

Liang, B., Lehmann, J., Solomon, D., Sohi, S., Thies, J. E., Skjemstad, J. O., et al. (2008). Stability of biomass-derived black carbon in soils. *Geochim. Cosmochim. Acta* 72, 6069–6078. doi: 10.1016/j.gca.2008.09.028

Lowe, L. E. (1978). "Carbohydrates distribution in soil," in *Soil Organic Matter*, eds M. Schnitzer and S. U. Khan (Amsterdam: Elsevier), 67–74.

McBeath, A. V., Wurster, C. M., and Bird, M. I. (2015). Influence of feedstock properties and pyrolysis conditions on biochar carbon stability as determined by hydrogen pyrolysis. *Biomass Bioenergy* 73, 155–173. doi: 10.1016/j.biombioe.2014.12.022

Merckx, R., den Hartog, A., and van Veen, J. A. (1985). Turnover of root-derived material and related microbial biomass formation in soils of different texture. *Soil Biol. Biochem.* 17, 565–569. doi: 10.1016/0038-0717(85)90026-4

Nelson, P. N., and Baldock, J. A. (2005). Estimating the molecular composition of a diverse range of natural organic materials from solid-state 13C NMR and elemental analyses. *Biogeochemistry* 72, 1–34. doi: 10.1007/s10533-004-0076-3

New, M., Lister, D., Hulme, M., and Makin, I. (2002). A high-resolution data set of surface climate over global land areas. *Clim. Res.* 21, 1–25. doi: 10.3354/cr021001

Nocentini, C., Certini, G., Knicker, H., Francioso, O., and Rumpel, C. (2010). Nature and reactivity of charcoal produced and added to soil during wildfire are particle-size dependent. *Org. Geochem.* 41, 682–689. doi: 10.1016/j.orggeochem.2010.03.010

Peters, W. J., and Neuenschwander, L. F. (1988). *Slash and Burn. Farming in the* Third *World Forest*. Moscow, ID: University of Idaho Press.

Pignatello, J. J., Uchimiya, M., Abiven, S., and Schmidt, M. W. I. (2015). "Evolution of biochar properties in soil," in *Biochar for Environmental Management - Science, Technology and Implementation*, eds J. Lehmann and S. Joseph (London: Routledge), 195–233.

Preston, C. M., and Schmidt, M. W. I. (2006). Black (pyrogenic) carbon: a synthesis of current knowledge and uncertainties with special consideration of boreal regions. *Biogeosciences* 3, 397–420. doi: 10.5194/bg,-3-397-2006

QGIS Development Team (2015). *QGIS Geographic Information System*. Available online at: http://qgis.osgeo.org

Randerson, J. T., Chen, Y., van der Werf, G. R., Rogers, B. M., and Morton, D. C. (2012). Global burned area and biomass burning emissions from small fires. *J. Geophys. Res.* 117, G04012. doi: 10.1029/2012JG002128

R Core Team (2015). *R: A Language and Environment for Statistical Computing*. Available online at: https://www.r-project.org

Rubel, F., and Kottek, M. (2010). Observed and projected climate shifts 1901-2100 depicted by world maps of the Köppen-Geiger climate classification. *Meteorol. Zeitschrift* 19, 135–141. doi: 10.1127/0941-2948/2010/0430

Saiz, G., Goodrick, I., Wurster, C. M., Zimmermann, M., Nelson, P. N., and Bird, M. I. (2014). Charcoal re-combustion efficiency in tropical savannas. *Geoderma* 219–220, 40–45. doi: 10.1016/j.geoderma.2013.12.019

Santín, C., Doerr, S. H., Kane, E. S., Masiello, C. A., Ohlson, M., de la Rosa, J. M., et al. (2016). Towards a global assessment of pyrogenic carbon from vegetation fires. *Glob. Chang. Biol.* 22, 76–91. doi: 10.1111/gcb.12985

Santín, C., Doerr, S. H., Preston, C., and Bryant, R. (2013). Consumption of residual pyrogenic carbon by wildfire. *Int. J. Wildl. Fire* 22, 1072–1077. doi: 10.1071/WF12190

Santín, C., Doerr, S. H., Preston, C. M., and González-Rodríguez, G. (2015). Pyrogenic organic matter production from wildfires: a missing sink in the global carbon cycle. *Glob. Chang. Biol.* 21, 1621–1633. doi: 10.1111/gcb.12800

Schmidt, M. W. I., Skjemstad, J. O., Czimczik, C. I., Glaser, B., Prentice, K. M., Gelinas, Y., et al. (2001). Comparative analysis of black carbon in soils. *Global Biogeochem. Cycles* 15, 163–167. doi: 10.1029/2000GB001284

Schneider, M. P. W., Hilf, M., Vogt, U. F., and Schmidt, M. W. I. (2010). The benzene polycarboxylic acid (BPCA) pattern of wood pyrolyzed between 200°C and 1000°C. *Org. Geochem.* 41, 1082–1088. doi: 10.1016/j.orggeochem.2010.07.001

Schneider, M. P. W., Smittenberg, R. H., Dittmar, T., and Schmidt, M. W. I. (2011). Comparison of gas with liquid chromatography for the determination of benzenepolycarboxylic acids as molecular tracers of black carbon. *Org. Geochem.* 42, 275–282. doi: 10.1016/j.orggeochem.2011.01.003

Singh, N., Abiven, S., Torn, M. S., and Schmidt, M. W. I. (2012). Fire-derived organic carbon in soil turns over on a centennial scale. *Biogeosciences* 9, 2847–2857. doi: 10.5194/bg-9-2847-2012

Six, J., Conant, R. T., Paul, E. A., and Paustian, K. (2002). Stabilization mechanisms of soil organic matter: implications for C-saturatin of soils. *Plant Soil* 241, 155–176. doi: 10.1023/A:1016125726789

Skjemstad, J. O., Clarke, P., Taylor, J. A., Oades, J. M., and McClure, S. G. (1996). The chemistry and nature of protected carbon in soil. *Aust. J. Soil Res.* 34, 251–271. doi: 10.1071/SR9960251

Sørensen, L. H. (1972). Stabilization of newly formed amino acid metabolites in soil by clay minerals. *Soil Sci.* 114, 5–11. doi: 10.1097/00010694-197207000-00002

Thevenot, M., Dignac, M. F., and Rumpel, C. (2010). Fate of lignins in soils: a review. *Soil Biol. Biochem.* 42, 1200–1211. doi: 10.1016/j.soilbio.2010.03.017

Tinkham, W. T., Smith, A. M. S., Higuera, P. E., Hatten, J. A., Brewer, N. W., and Doerr, S. H. (2016). Replacing time with space: using laboratory fires to explore the effects of repeated burning on black carbon degradation. *Int. J. Wildl. Fire* 25, 242–248. doi: 10.1071/WF15131

Wiedemeier, D. B., Hilf, M. D., Smittenberg, R. H., Haberle, S. G., and Schmidt, M. W. I. (2013). Improved assessment of pyrogenic carbon quantity and quality in environmental samples by high-performance liquid chromatography. *J. Chromatogr. A*1304, 246–250. doi: 10.1016/j.chroma.2013.06.012

Wiedner, K., and Glaser, B. (2015). “Traditional use of biochar,” in *BIochar for Environmental Management - Science and Technology*, eds J. Lehmann and S. Joseph (London: Routledge), 15–37.

Zhao, M., Heinsch, F. A., Nemani, R. R., and Running, S. W. (2005). Improvements of the MODIS terrestrial gross and net primary production global data set. *Remote Sens. Environ.* 95, 164–176. doi: 10.1016/j.rse.2004.12.011

Manuscript 2

Long lasting influence of pyrogenic carbon on soil organic carbon and drivers of its content in forest soils

Moritz Reisser[1], Philippa Ascough[2], Beatriz González-Domínguez[1,3], Lukas Wacker[4], Frank Hagedorn[5], Pascal A. Niklaus[3], Samuel Abiven[1*]

1-Department of Geography, Soil Science and Biogeochemistry Unit, University of Zurich (UZH), Winterthurerstrasse 190, 8057 Zurich, Switzerland

2-NERC Radiocarbon Facility, Scottish Universities Environmental Research Centre (SUERC), University of Glasgow, Rankine Avenue, G75 0QF, East Kilbride, UK

3-Department of Evolutionary Biology and Environmental Studies, University of Zurich (UZH), Winterthurerstrasse 190, 8057 Zurich, Switzerland

4-Department of Physics, Laboratory of Ion Beam Physics, Swiss Federal Institute of Technology (ETH), Otto-Stern-Weg 5, 9083 Zurich, Switzerland

5-Forest Soils and Biogeochemistry, Swiss Federal Institute for Snow, Forest and Landscape Research (WSL), Zürcherstrasse 111, 8903 Birmensdorf, Switzerland

*Corresponding author: samuel.abiven@geo.uzh.ch

Contributions: S.A. and M.R. conceived the study. S.A., B.G-D., P.N. and F.H. developed the initial experimental design and provided additional data. L.W. provided the ^{14}C data. M.R. and P.L.A. conducted the laboratory work. S.A., P.L.A and M.R. interpreted the data and all authors contributed to the writing of the manuscript.

Submitted: PLOS One, June 2018

Keywords: pyrogenic carbon, stabilization, hydrogen pyrolysis, benzene polycarboxylic acids, forest soils, priming, soil properties

Abstract

Pyrogenic organic carbon (PyC) from wildfires is an important, but poorly quantified component of the global carbon cycle and a significant soil C sink. PyC is also a driver of total soil C persistence because of its very high turnover time. Despite this, the drivers of PyC content are not well disentangled at the ecosystem level. Neither do we understand how PyC affects the decadal to centennial turnover of non-PyC soil carbon, impeding not only effective modelling of carbon feedbacks but also potential actions against climate change. Here, we use a network of 54 Swiss forest sites, ideally suited to statistically decorrelate putative climatic and regional drivers. We apply two independent techniques to demonstrate that soil properties (clay content and pH) are the key controls of soil PyC contents. Soil incubations and soil ^{14}C data also reveal that a slow SOC turnover is associated with relatively larger amounts of highly resistant, polyaromatic PyC even where total PyC content is low. These findings suggest that small quantities of PyC lead to a much stronger stabilization of C in soils than previously thought, meaning the benefits of PyC for climate change mitigation may have been underestimated.

Introduction

Pyrogenic organic carbon (PyC) is the product of the incomplete combustion of biomass, e.g. via wildfires. PyC is ubiquitous in soils[1], globally making up 13.7 % of soil organic content[2], meaning it already represents around 50 % of the compounds which can be isolated chemically or physically from soil matrices[2]. PyC persists in soils for centuries to millenia[3–5] making a substantial contribution to the long turnover time of soil organic carbon (SOC). Therefore, the intentional (e.g. as biochar amendment[6]) or unintentional (via wildfires[7]) addition of PyC to soils might constitute an important soil sink for C; natural fires alone are estimated to result in a global sequestration of 114-380 Tg y^{-1} in PyC[8]. This sink would further increase with future expected increases in fire frequency[9]. PyC thus needs to be considered in climate change modelling and management as it provides valuable opportunities in mitigation of these changes. However, there is large uncertainty regarding PyC turnover times, which can vary by two orders of magnitude, and are highly likely to depend on multiple ecosystem properties that are difficult to disentangle[10,11]. An important body of literature highlights the different stabilization mechanisms of PyC in the field and the laboratory[12–16]. However, it is difficult to extrapolate such results to other spatial scales, due to firstly a lack of regional scale studies (tens to hundreds of kilometres),

even though knowledge on the controls of PyC content and persistence at these scales is critical as these are particularly relevant to policy makers. Secondly, PyC can also have an effect on non-PyC decomposition[17,18], further complicating prediction of C dynamics. This process is not well understood, particularly at decadal to centennial time scales. Given that PyC represents such a large C pool, these gaps in understanding affect our estimations of C persistence in soils[18]. Improving our knowledge of these processes and mechanisms will not only foster modelling approaches but also provide a better basis for management practices aiming at SOC conservation and climate change mitigation.

Here, we use a set of 54 Swiss forest sites established in a previous study (González-Domínguez et al., in rev.). These sites were selected in a way that minimized the statistical correlations of different putative drivers of soil C turnover (in particular climate, soil properties and landform; see also supplementary material). On these sites, we used two PyC quantification methods to show that over large environmental and soil property gradients, PyC content is driven mainly by precipitation and soil properties (e.g. pH and clay content). We further present evidence that PyC leads to a significant and important long lasting reduction of SOC turnover.

The sites were selected from a forest soil database of over 1000 soil profiles including information on climate (mean average air temperature and dryness index (more information on this index and the methodology in general is given in the supplementary information), both 1981-2010), soil properties (pH, clay content [%]) and landform (slope [%], orientation (N-E-S-W)). A principal coordinate analysis was used to aggregate data related to soil properties and landform to two orthogonal variables (principal coordinates). The overall study area was heterogeneous with respect to vegetation, climate, and parent materials; to avoid confounding these factors we used large biogeographical regions (BGR) as blocks. The final set of sites was selected so that the effects of all included variables (BGR, moisture, temperature, principal coordinates 1 and 2) were close to orthogonality, i.e. they were statistically nearly independent in multiple linear regression models.

Two turnover times were calculated based on an incubation and on radiocarbon (^{14}C) data. A short-term turnover time of the bulk SOC (τ_{short}) was calculated from a 181-

day incubation experiment of the samples from the 54 sites, representing mainly the labile part of SOC. A long-term in situ turnover time (τ_{long}) was calculated from the ^{14}C signature of the bulk SOC (González-Domínguez et al., in rev.). This τ_{long} represents an average turnover of all SOC in the system[19]. τ_{long} and τ_{short} were uncorrelated, suggesting that they capture different properties of the systems.

We used two methods to quantify and characterize PyC: the benzene-polycarboxylic acid (BPCA) molecular marker method[20] and hydrogen pyrolysis[21,22] (HyPy). BPCA has been one of the most frequently used methods for PyC determination over the last two decades[2] and is semi-quantitative[23]. Four groups of molecules are obtained by the analysis, B3CA, B4CA, B5CA and B6CA, with aromaticity and degree of condensation indicated by the molecule-group index (figure 1)[24]. The BPCA method selectively quantifies chemically functional parts of PyC; material which lacks such functionalities such as graphite or strongly condensed soot remains undetected[23,24]. On the other hand, HyPy is strictly quantitative and measures all PyC with >7 coherent rings[21,22]. These methods are ideally suited, and can be robustly calibrated against each other in different environmental matrixes[25]. For this study we also performed an independent method comparison specific to our dataset (given in the supplementary information).

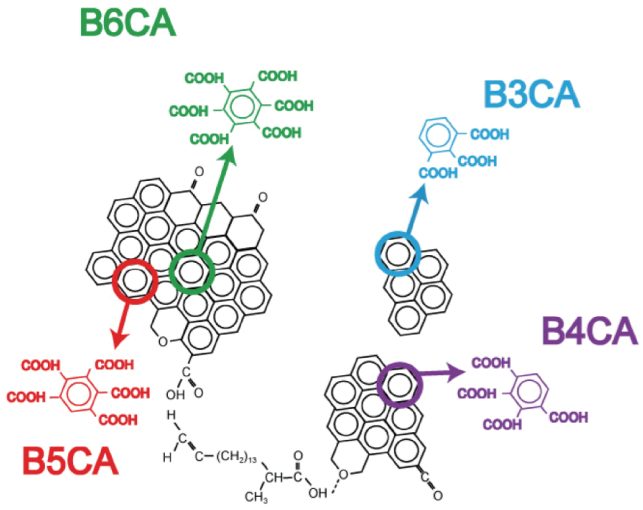


Figure 1: Theoretical structure of PyC resulting in BPCA marker compounds. The higher the index number of the marker, the more benzene rings were surrounding it before digestion. The HyPy method would detect both large molecules, which result here in B4CA to B6CA markers, but not the one, which results here in a B3CA marker. Modified from ref 20.

Measured contents of PyC

In the 54 soils studied, PyC contents in the SOC (table 1) are rather low with 0.6 to 4.7 % and 1.4 to 9.9 % for PyC_{BPCA} and PyC_{HyPy}, respectively (with a single exception, see below). In comparison, other studies at larger spatial scales reported contents of up to 35 %[26] or even up to 51 % in Australia[27,28]. This large mismatch is surprising, because even though the spatial extent of our study was much smaller, the ranges in climatic conditions and soil properties were greater than in most other studies[14,15,29] (e.g. samples were taken in climate zones ranging from Mediterranean (Southern Switzerland) to boreal (high altitude) climates).

Table 1: Ranges and distributions of the different variables in the dataset. τ_{short} is the turnover time based on the 181 days incubation experiment and τ_{long} is the turnover time based on the ^{14}C of the bulk SOC.

Variable	Min.	1st Quar.	Median	Mean	3rd Quar.	Max.
PyC_{BPCA} [g kg^{-1} SOC]	0.64	1.53	1.87	2.07	2.28	9.23
PyC_{HyPy} [g kg^{-1} SOC]	1.41	2.82	3.35	4.62	4.66	31.4
Mean annual temperature [°C]	1.1	6.5	8.1	7.7	9.4	11.8
Mean monthly precipitation [mm]	58.7	92.7	109.0	112.9	128.6	184.7
pH	2.83	3.97	4.93	4.98	5.79	7.01
Clay content [%]	4.8	12.3	19.3	21.6	26.7	60.2
Slope [%]	0.07	12.1	26.9	26.6	39.4	76.8
τ_{short} [yr	5.1	7.6	9.0	10.4	12.2	28.8
τ_{long} [yr]	66	126	143	189	177	1143

The reason for the consistently low PyC contents is probably the low fire-frequency found here as in most temperate and boreal ecosystems[30]. Literature on fire activity in Switzerland suggests that chances of recent fires were very low. In the last century the fire rotation period was not shorter than between 270 and 800 years even in the most wildfire-prone zones in South Switzerland, due to human protective measures[31]. Only one of the 54 sites has experienced a very recent fire (<5 years before sampling). The PyC content from this site is with 9.2 % and 24.5 % for PyC_{BPCA} and

PyC_{HyPy}, respectively 4 to 7 times higher contents in the SOC than the average of the remaining sites.

Ecosystem properties as drivers of PyC content

Our data shows that long-term variables of climate and soil properties are important and significant drivers of PyC contents in SOC (table 2). Moisture was significant with $P < 0.05$ for PyC_{HyPy}, revealing that PyC contents were ~20 % smaller in the drier half of the soils than in the wetter half. pH was positively correlated to PyC_{HyPy} ($P < 0.01$) and clay content was positively correlated to PyC_{BPCA} ($P < 0.01$). No other driver could be detected to explain another significant portion of the variance in the measured PyC values.

Table 2: Results from the ANOVA to investigate the influence of the different drivers on the PyC contents. PyC_{BPCA} and PyC_{HyPy} are the PyC contents [g kg^{-1} SOC] measured with the BPCA and the HyPy method, respectively. BGR is the biogeographical region, MI is the moisture index (two-level categorical variable: moist, dry), TI is the temperature index (two-level categorical variable: warm, cold), MI x TI is the interaction between the two. Orientation is four-level categorical (N,E,S,W). PyC_{HyPy} and clay content were log-transformed in the analysis to meet the requirement of normality. Numbers in the driver model represent the lowest p-values found over all positions and number in brackets indicate the number of times that a p-value <0.05 was found. From the driver model, we only considered the results, which had at least once a p-value < 0.01 and at least 5 of 6 times a p-value < 0.05.

PyC content	**Significance of drivers**					
Main model	BGR	TI	MI	TIxMI	pco1	pco2
PyC_{BPCA} [g kg^{-1} SOC]	0.38	0.8	0.43	0.29	0.23	0.69
PyC_{HyPy} [g kg^{-1} SOC]	0.06	0.57	0.012	0.26	0.024	0.09

Driver model				
	pH	clay [%]	slope [%]	orientation
PyC_{BPCA} [g kg^{-1} SOC]	0.048 (3)	0.002 (5)	0.45 (0)	0.31 (0)
PyC_{HyPy} [g kg^{-1} SOC]	0.002 (5)	0.038 (1)	0.23 (0)	0.07 (0)

Our finding that precipitation is a key driver of PyC content supports the general assumption that climate is very important for PyC dynamics[32]; however on a global scale and covering all methods, mainly temperature has previously been identified as important[2]. We find here at a smaller scale that moisture is the dominant driver of

PyC, without any apparent influence from temperature. Similar relationships with climate have been observed for total SOC[33]. Global or large-scale studies on SOC dynamics show a larger influence of temperature[34], while regional or local studies show a larger influence of precipitation[35,36]. A faster decomposition or flushing of labile SOC with increased precipitation could lead to a relative accumulation of PyC and thus explain our results. Precipitation correlates directly to PyC_{HyPy}, and hence overall PyC content, meaning that the mechanisms behind this relationship are largely independent of the chemical structure of the PyC, further supporting that the SOC is actually affected more by the precipitation than PyC.

The positive correlation between pH and PyC_{HyPy} content is in agreement with other studies[2,37]. Our results suggest that the relationship with pH applies mainly for PyC but not for the bulk SOC, because we examine only relative PyC contents in SOC. Other studies could not detect a significant correlation between pH and bulk SOC across large environmental gradients[33,38]. It is not clear how soil pH and PyC content are related. On one hand, PyC itself can raise the pH of the surrounding soil, since its own pH is usually above 8[39]. However, there is evidence that this liming effect lasts no longer than a few years[40]. On the other hand, high pH was shown to also have an effect on PyC. Under alkaline conditions ref [37] found, that fragmentation of PyC is strongly increased. A high fragmentation rate means a faster physical breakdown of the material, resulting in both a higher potential transport into and within the soil as well as a higher specific surface area. On the other hand, soils with high pH may slow down the decay of PyC, due to the stabilization by carbonates, similarly observed for SOC[41]. Both mechanisms would lead to a higher potential stabilization in fine fractions such as clay[42], supporting our findings here. Since we found no significant correlation of pH and PyC_{BPCA}, but only with PyC_{HyPy}, we can argue that the chemical structure is not important for these processes, supporting the assumption that physical processes like fragmentation are mainly relevant here.

Clay content was significantly positively related to PyC_{BPCA} content ($P < 0.01$). A similar positive correlation has been found before in other studies[2,10,43] and can be explained by the high capacity of PyC to form organo-mineral interactions with clay[44,45] because of its high reactive and specific surface. These interactions (adsorption, covalent binding, complexation) can protect the organic molecules from chemical degradation and rely on the chemical structures of both the minerals and

the organic molecules. This is why only the PyC_{BPCA} (which measures chemically reactive PyC[24]) but not PyC_{HyPy} shows a significant relationship.

Landform is one of the main drivers of soil formation and hence another important factor in SOC dynamics. Here we did not find any significant relationships between slope or orientation and soil PyC content, although PyC could be preferentially eroded versus other SOC[46]. Preferential erosion would likely take place rapidly after wildfires, when the material still lies on the soil surface. However, we do not see this on the spatial and temporal scales of this study, thus over decades to centuries, landform probably does not play an important role in the selective preservation or degradation of PyC.

In summary, drivers that are constant over long timescales are the ones that mainly correlate with the content of PyC. Soil properties such as pH and clay are environmental properties, which integrate a more or less constant influence over the whole life span of PyC in soils. Equally, climate seems to have a certain effect on the PyC persistence through the moisture regime as it is also fairly constant on timescales of centuries. Events which directly influence PyC deposition, e.g. fires and post-fire erosion (even though landform is very constant, post-fire erosion is not), are probably very important in the short-term, but we could not find evidence that they still drive long-term PyC content. The negative correlation with moisture suggests stabilizing factors are more important for long-term PyC contents than input rates, as we found lower PyC in drier soils where more frequent fires are expected.

Relation of short- and long-term SOC turnover time with PyC

We observed correlations of τ_{short} and τ_{long} with PyC_{BPCA}, which were most pronounced with the BPCA derivatives B5CA and B6CA, respectively. B5CA indicates already condensed and aromatic structures, but originates from an edge, while B6CA implicitly originates from the inside of aromatic sheets, indicating an even higher aromaticity and degree of condensation (figure 1). Pearson's product moment correlation resulted in $r = 0.31$ and $P = 0.025$ for B5CA and $\tau_{short,}$ corresponding to higher turnover times with higher amounts of PyC_{BPCA}. Similarly, correlation of B6CA with τ_{long} was 0.31 with an adjacent *P*-value of 0.024. PyC_{HyPy} was not correlated with either of the two turnover times.

The relationship between τ_{short} and B5CA is unexpected for two reasons. First, τ_{short} was calculated based on SOC mineralisation in a 6-month incubation experiment, resulting in decadal turnover times (5 – 29 years). Meanwhile, PyC has a turnover of centuries to millennia[3–5]. Second, PyC content in SOC was <10% in all samples (except the outlier) and B5CA only represents a fraction (23 – 51 %) of total PyC, therefore it cannot significantly dilute the SOC to explain the results.

The influence of an external substrate input on the turnover or mineralization rate of the residual SOC is usually described as priming[47,48]. Historically, a priming effect, either positive or negative, was understood as a short-term process, occurring over the course of some days to months, and most research has focused on these timescales[47,48]. However, our results support recent findings that PyC could affect mineralization rates of bulk SOC over years or even decades[17,18,49]. In our study, the input of PyC happened decades to centuries ago. Although it is not possible to calculate a priming effect due to lacking control samples and ages of PyC, our results suggest that there is a long-term reduction in SOC turnover with increasing content of PyC in soils. Therefore, we can interpret the correlation between τ_{short} and B5CA as demonstrating an extremely long lasting priming effect. Similar interpretations have been made from the famous Terra Preta de Indios soils in the Amazon[50], where extraordinarily high SOC contents and current turnover times result from centuries-old addition of PyC.

We assume that a negative priming on such timescales could only be caused by stabilization of labile SOC through PyC[49]. The fact that we only found a relationship between PyC_{BPCA} and τ_{short} but not PyC_{HyPy} shows that chemical structure of PyC (aromaticity and functional groups) plays a key role in SOC stabilization.

Linear regression showed a 4.5 year increase of τ_{short} (to be compared to the bulk range of 5-29 years) for every increase in B5CA of 10 g kg^{-1} SOC, highlighting the quantitative relevance of even small amounts of PyC on bulk SOC stability.

It is also the first time that a relationship between PyC_{BPCA}, in the form of B6CA, with τ_{long} of bulk SOC was observed. Timescales of the turnover of PyC and τ_{long} (mean = 189 yr) are much more comparable than in the case of τ_{short}. Since τ_{long} is based on bulk soil ^{14}C it is including PyC, as turnover times of bulk and PyC are in the same range. It is likely that a large τ_{long}, reflected by an old mean age of the bulk SOC would lead to a relative accumulation of very persistent C, such as PyC. This is consistent with the correlation between B6CA and τ_{long}, and the fact that B6CA represents the most persistent part of PyC_{BPCA}[23,24]. In addition, similar mechanisms

could be at work as in the case of τ_{short}, i.e. the abundance of very aromatic and condensed PyC (represented by the B6CA) causes a decrease in turnover of even old and persistent SOC.

Our results highlight the importance of PyC for SOC dynamics and the global C cycle, as a potential sink itself, and a driver of SOC stabilisation. We show that even small amounts of PyC are significantly correlated to SOC turnover at decadal to centennial timescales. Both quantity and chemical structure of PyC are decisive factors in their direct and indirect influence on SOC turnover and stocks. The relative contents of PyC in SOC are mainly determined by ecosystem properties like moisture and pH on the local scale, while the chemical structure is determining the potential persistence of PyC through e.g. stabilization by clay minerals as well as its influence on SOC stability.
Pyrogenic C needs to be taken into account in estimating and predicting current and future C balances.

Acknowledgement

We thank the Federal Institute for Forest, Snow and Landscape (WSL), in particular L. Walthert for the provision of the database. This research is supported by the University of Zurich through the University Research Priority Program Global Change and Biodiversity (URPP GCB).

Author Contributions

S.A. and M.R. conceived the study. S.A., B.G-D., P.N. and F.H. developed the initial experimental design and provided additional data. L.W. provided the ^{14}C data. M.R. and P.L.A. conducted the laboratory work. S.A., P.L.A and M.R. interpreted the data and all authors contributed to the writing of the manuscript.

Methods

Site Selection. The detailed description of the stepwise procedure to achieve near-orthogonal drivers is given in in the supplementary information.

The turnover times from the incubation study were calculated with the ratio of SOC stocks to the output flux[51] determined with NaOH traps over the course of 181 days. The second turnover time was modelled using the carbonate-free bulk soil ^{14}C

signal[52]. The model is based on the assumption of steady-state conditions and does not account for lag-times. More detailed description is given in (González-Domínguez et al. in rev.).

The benzene polycarboxylic acids (BPCA) molecular marker method is used to quantify PyC in soils and has been widely applied[53–56]. The detailed procedure has been described by ref. 20. Briefly, the soil samples are treated with a surplus of nitric acids (8 h, 170 °C). The digested extract is then purified using cation exchange resin and, after freeze drying, solid phase extraction. They are then derivatised and analysed on a liquid chromatograph. The acids with 3, 4, 5 and 6 carboxyl functions (B3CA, B4CA, B5CA, B6CA) are identified, quantified and summed up for the total BPCA amount.

Hydrogen Pyrolysis (HyPy) quantifies all aromatic fire residues having >7 coherent aromatic rings. Here, an additional HCl (0.1 M) pre-treatment was used before the established method for the samples, which contained carbonates. The method is described in detail in ref. 21,22. Briefly, around 100 mg of sample are loaded with a Mo catalyst using a aqueous/methanol (1:1) solution of ammonium dioxydithiomolybdate [$(NH_4)_2MoO_2S_2$]. Catalyst weight is around 10 % sample weight, which results of a Mo loading of around 1 %. Samples were then placed in the hypy reactor, pressurized with H_2 to 15 MPa with a sweep gas flow of 5 L min^{-1} and heated with a pre-programmed temperature profile. Samples are initially heated at a rate of 300 °C min^{-1} to 250 °C, then heated at a rate of 8 °C min^{-1} until a final hold temperature of 550 °C for 2 min.

pH, total soil organic carbon (SOC) & other data. Soil pH ($CaCl_2$) was measured on 40˚C dried composite subsamples. Part of these subsamples were also milled and fumigated with HCl to quantify TOC by Elemental Analysis (vario MICRO cube, Elementar, Germany). The rest of data, were sourced from the Federal Institute for Forests, Snow and Landscape (WSL) soil database.

Statistics:

All statistical analyses were performed with R statistical software (R 3.1.1 ref. [57]) including the package “lattice”.

We used linear multiple regression models summarized by analysis of variance (ANOVA) to test for significant effects of explanatory variables. To test for climatic variables, summarized soil properties (pco1) and landform (pco2) we fitted the explanatory variables sequentially, in the order *BGR + MI + TI + MI×TI + pco1 + pco2*, where BGR is a block factor coding for biogeographical region, MI and TI are indices for moisture and temperature, respectively, and pco1 and pco2 are the principal coordinates from the site selection. (more details of the statistical design are given in (González-Domínguez et al. in rev.). PyC_{HyPy}, as well as clay content were log-transformed to meet the criteria of normally distributed residuals in the test.

To test for specific drivers we fitted the explanatory variables sequentially with varying order to make sure significant results were independent. From this model, we only considered the results, which had at least once a p-value < 0.01 and at least 5 of 6 times a p-value < 0.05. A summary of all combinations for the considered variables pH and clay is given in supplement 2.

References:

1. Schmidt, M. W. I., Noack, A. G. & Osmond, G. Black carbon in soils and sediments: Analysis , distribution , implications , and current challenges. *Global Biogeochem. Cycles* **14,** 777–793 (2000).
2. Reisser, M., Purves, R. S., Schmidt, M. W. I. & Abiven, S. Pyrogenic Carbon in Soils: A Literature-Based Inventory and a Global Estimation of Its Content in Soil Organic Carbon and Stocks. *Front. Earth Sci.* **4,** 1–14 (2016).
3. Singh, N., Abiven, S., Torn, M. S. & Schmidt, M. W. I. Fire-derived organic carbon in soil turns over on a centennial scale. *Biogeosciences* **9,** 2847–2857 (2012).
4. Hammes, K., Torn, M. S., Lapenas, a. G. & Schmidt, M. W. I. Centennial black carbon turnover observed in a Russian steppe soil. *Biogeosciences Discuss.* **5,** 661–683 (2008).
5. Bird, M. I., Wynn, J. G., Saiz, G., Wurster, C. M. & McBeath, A. The Pyrogenic Carbon Cycle. *Annu. Rev. Earth Planet. Sci.* **43,** 273–98 (2015).
6. Lehmann, J. & Joseph, S. *Biochar for Environmental Management - Science, Technology and Implementation*. (Routledge, 2015).

7. Santín, C., Doerr, S. H., Preston, C. M. & González-Rodríguez, G. Pyrogenic organic matter production from wildfires: a missing sink in the global carbon cycle. *Glob. Chang. Biol.* **21,** 1621–1633 (2015).
8. Santín, C. *et al.* Towards a global assessment of pyrogenic carbon from vegetation fires. *Glob. Chang. Biol.* **22,** 76–91 (2016).
9. IPCC. *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*. (2013).
10. Czimczik, C. I. & Masiello, C. a. Controls on black carbon storage in soils. *Global Biogeochem. Cycles* **21,** (2007).
11. Schmidt, M. W. I. *et al.* Persistence of soil organic matter as an ecosystem property. *Nature* **478,** 49–56 (2011).
12. Vasilyeva, N. A. *et al.* Pyrogenic carbon quantity and quality unchanged after 55 years of organic matter depletion in a Chernozem. *Soil Biol. Biochem.* **43,** 1985–1988 (2011).
13. Singh, N. *et al.* Transformation and stabilization of pyrogenic organic matter in a temperate forest field experiment. *Glob. Chang. Biol.* **20,** 1629–1642 (2014).
14. Soucémarianadin, L. N., Quideau, S. a. & MacKenzie, M. D. Pyrogenic carbon stocks and storage mechanisms in podzolic soils of fire-affected Quebec black spruce forests. *Geoderma* **217–218,** 118–128 (2014).
15. Cheng, C. H., Lehmann, J., Thies, J. E. & Burton, S. D. Stability of black carbon in soils across a climatic gradient. *J. Geophys. Res. Biogeosciences* **113,** 1–10 (2008).
16. Lehmann, J., Czimczik, C. I., Laird, D. & Sohi, S. in *Biochar for Environmental Management - Science and Technology* (eds. Lehmann, J. & Joseph, S.) 189 (earthscan, 2009).
17. Woolf, D. & Lehmann, J. Modelling the long-term response to positive and negative priming of soil organic carbon by black carbon. *Biogeochemistry* **111,** 83–95 (2012).
18. Maestrini, B., Nannipieri, P. & Abiven, S. A meta-analysis on pyrogenic organic matter induced priming effect. *GCB Bioenergy* **7,** 577–590 (2014).
19. Trumbore, S. Age of soil organic matter and soil respiration: Radiocarbon constraints on belowground C dynamics. *Ecol. Appl.* **10,** 399–411 (2000).

20. Wiedemeier, D. B. *et al.* Characterization, Quantification and Compound-specific Isotopic Analysis of Pyrogenic Carbon Using Benzene Polycarboxylic Acids (BPCA). *J. Vis. Exp* (2016). doi:10.3791/53922
21. Ascough, P. L. *et al.* Hydropyrolysis as a new tool for radiocarbon pre-treatment and the quantification of black carbon. *Quat. Geochronol.* **4,** 140–147 (2009).
22. Meredith, W. *et al.* Assessment of hydropyrolysis as a method for the quantification of black carbon using standard reference materials. *Geochim. Cosmochim. Acta* **97,** 131–147 (2012).
23. Glaser, B., Haumaier, L., Guggenberger, G. & Zech, W. Black carbon in soils : the use of benzenecarboxylic acids as specific markers. *Org. Geochem.* **29,** 811–819 (1998).
24. Wiedemeier, D. B. *et al.* Aromaticity and degree of aromatic condensation of char. *Org. Geochem.* **78,** 135–143 (2015).
25. Cotrufo, F. M. *et al.* Quantification of pyrogenic carbon in the environment: An integration of analytical approaches. *Org. Geochem.* **100,** 42–50 (2016).
26. Forbes, M. S., Raison, R. J. & Skjemstad, J. O. Formation, transformation and transport of black carbon (charcoal) in terrestrial and aquatic ecosystems. *Sci. Total Environ.* **370,** 190–206 (2006).
27. Lehmann, J. *et al.* Australian climate–carbon cycle feedback reduced by soil black carbon. *Nat. Geosci.* **1,** 832–835 (2008).
28. Skjemstad, J. O., Dalal, R. C., Janik, L. J. & McGowan, J. A. Changes in chemical nature of soil organic carbon in Vertisols under wheat in south-east Queensland. *Aust. J. Soil Res.* **39,** 343–359 (2001).
29. Jauss, V., Johnson, M., Krull, E., Daub, M. & Lehmann, J. Pyrogenic carbon controls across a soil catena in the Pacific Northwest. *Catena* **124,** 53–59 (2015).
30. Archibald, S., Lehmann, C. E. R., Gómez-dans, J. L. & Bradstock, R. A. Defining pyromes and global syndromes of fire regimes. *Proc. Natl. Acad. Sci. U. S. A.* **110,** 6442–6447 (2013).
31. Tinner, W., Conedera, M., Ammann, B. & Lotter, A. F. A. F. Fire ecology north and south of the Alps since the last ice age. *The Holocene* **15,** 1214–1226 (2005).
32. Glaser, B. & Amelung, W. Pyrogenic carbon in native grassland soils along a climosequence in North America. *Global Biogeochem. Cycles* **17,** (2003).

33. Doetterl, S. *et al.* Soil carbon storage controlled by interactions between geochemistry and climate. *Nat. Geosci.* **8,** 780–783 (2015).
34. Davidson, E. A. & Janssens, I. A. Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. *Nature* **440,** 165–173 (2006).
35. Giardina, C. P., Litton, C. M., Crow, S. E. & Asner, G. P. Warming-related increases in soil CO2 efflux are explained by increased below-ground carbon flux. *Nat. Clim. Chang.* **4,** 822–827 (2014).
36. Moyano, F. E. *et al.* The moisture response of soil heterotrophic respiration: Interaction with soil properties. *Biogeosciences* **9,** 1173–1182 (2012).
37. Braadbaart, F., Poole, I. & van Brussel, A. A. Preservation potential of charcoal in alkaline environments: an experimental approach and implications for the archaeological record. *J. Archaeol. Sci.* **36,** 1672–1679 (2009).
38. Chen, S., Huang, Y., Zou, J. & Shi, Y. Mean residence time of global topsoil organic carbon depends on temperature, precipitation and soil nitrogen. *Glob. Planet. Change* **100,** 99–108 (2013).
39. Ippolito, J. A., Spokas, K. A., Novak, J. M., Lentz, R. D. & Cantrell, K. B. in *Biochar for Environmental Management - Science, Technology and Implementation* (eds. Lehmann, J. & Joseph, S.) 139–163 (Routledge, 2015).
40. Yuan, J. H. & Xu, R. K. The amelioration effects of low temperature biochar generated from nine crop residues on an acidic Ultisol. *Soil Use Manag.* **27,** 110–115 (2011).
41. Rowley, M. C., Grand, S. & Verrecchia, É. P. Calcium-mediated stabilisation of soil organic carbon. *Biogeochemistry* **137,** 27–49 (2017).
42. Nocentini, C., Certini, G., Knicker, H., Francioso, O. & Rumpel, C. Nature and reactivity of charcoal produced and added to soil during wildfire are particle-size dependent. *Org. Geochem.* **41,** 682–689 (2010).
43. Torn, M. S., Trumbore, S. E., Chadwick, O. A., Vitousek, P. M. & Hendricks, D. M. Mineral control of soil organic carbon storage and turnover. *Nature* **389,** 170–173 (1997).
44. Hassink, J. The capacity of soils to preserve organic C and N by their association with clay and silt particles. *Plant Soil* **191,** 77–87 (1997).
45. Six, J., Conant, R. T., Paul, E. A. & Paustian, K. Stabilization mechanisms of soil organic matter: Implications for C-saturation of soils. *Plant Soil* **241,** 155–176 (2002).

46. Rumpel, C. *et al.* Preferential erosion of black carbon on steep slopes with slash and burn agriculture. *Catena* **65,** 30–40 (2006).
47. Bingeman, C. W., Varner, J. E. & Martin, W. P. The Effect of the Addition of Organic Materials on the Decomposition of an Organic Soil. *Soil Sci. Soc. Am. J.* **17,** 34–38 (1953).
48. Kuzyakov, Y., Friedel, J. K. & Stahr, K. Review of mechanisms and quantification of priming effects. *Soil Biol. Biochem.* **32,** 1485–1498 (2000).
49. Zimmerman, A. R., Gao, B. & Ahn, M. Y. Positive and negative carbon mineralization priming effects among a variety of biochar-amended soils. *Soil Biol. Biochem.* **43,** 1169–1179 (2011).
50. Glaser, B., Haumaier, L., Guggenberger, G. & Zech, W. The 'Terra Preta' phenomenon: A model for sustainable agriculture in the humid tropics. *Naturwissenschaften* **88,** 37–41 (2001).
51. Sierra, C. A., Müller, M., Metzler, H., Manzoni, S. & Trumbore, S. E. The muddle of ages, turnover, transit, and residence times in the carbon cycle. *Glob. Chang. Biol.* **23,** 1763–1773 (2017).
52. Harkness, D. D., Harrison, A. F. & Bacon, P. J. The temporal distribution of 'bomb' 14C in a forest soil. *Radiocarbon* **28,** 328–337 (1986).
53. Schneider, M. P. W., Hilf, M., Vogt, U. F. & Schmidt, M. W. I. The benzene polycarboxylic acid (BPCA) pattern of wood pyrolyzed between 200°C and 1000°C. *Org. Geochem.* **41,** 1082–1088 (2010).
54. Wiedemeier, D. B., Brodowski, S. & Wiesenberg, G. L. B. Pyrogenic molecular markers: Linking PAH with BPCA analysis. *Chemosphere* **119,** 432–437 (2015).
55. Wiedemeier, D. B., Hilf, M. D., Smittenberg, R. H., Haberle, S. G. & Schmidt, M. W. I. Improved assessment of pyrogenic carbon quantity and quality in environmental samples by high-performance liquid chromatography. *J. Chromatogr. A* **1304,** 246–50 (2013).
56. Guggenberger, G. *et al.* Storage and mobility of black carbon in permafrost soils of the forest tundra ecotone in Northern Siberia. *Glob. Chang. Biol.* **14,** 1367–1381 (2008).
57. R Core Team. R: A Language and Environment for Statistical Computing. (2015).

Supplement Manuscript 2

Long lasting influence of pyrogenic carbon on soil organic carbon and drivers of its content in forest soils

Moritz Reisser[1], Philippa Ascough[2], Beatriz González-Domínguez[1,3], Lukas Wacker[4], Frank Hagedorn[5], Pascal A. Niklaus[3], Samuel Abiven[1*]

1-Department of Geography, Soil Science and Biogeochemistry Unit, University of Zurich (UZH), Winterthurerstrasse 190, 8057 Zurich, Switzerland

2-NERC Radiocarbon Facility, Scottish Universities Environmental Research Centre (SUERC), University of Glasgow, Rankine Avenue, G75 0QF, East Kilbride, UK

3-Department of Evolutionary Biology and Environmental Studies, University of Zurich (UZH), Winterthurerstrasse 190, 8057 Zurich, Switzerland

4-Department of Physics, Laboratory of Ion Beam Physics, Swiss Federal Institute of Technology (ETH), Otto-Stern-Weg 5, 9083 Zurich, Switzerland

5-Forest Soils and Biogeochemistry, Swiss Federal Institute for Snow, Forest and Landscape Research (WSL), Zürcherstrasse 111, 8903 Birmensdorf, Switzerland

*Corresponding author: samuel.abiven@geo.uzh.ch

Relation between the HyPy and the BPCA method

Even though the methods show partially different fractions of the PyC continuum, we found a clear correlation between the two (figure S1). The associated linear regression resulted in equation 1, where all values are in g kg-1 soil organic carbon (R^2 = 0.50, *p*-value = <0.001 for both intercept and slope). These results are in line with the recent method comparison(Cotrufo et al., 2016), which resulted in equation 2, also for forest soils.

$$PyC_{BPCA} = 0.206 * PyC_{HyPy} + 1.12 \quad [1]$$

$$PyC_{BPCA} = 0.23 * PyC_{HyPy} + 0.05 \quad [2]$$

The slopes of the linear regressions are very similar, even though different personnel measured them in different labs. In a previous method comparison this variability between different labs was shown to be much higher (Hammes et al., 2007). The intercept of our presented linear fit is however higher than the previous one and also strongly significant (*p*-value < 0.001). Both equations suggest, that the commonly used correction factor of 2.27 for PyC_{BPCA} (Glaser et al., 1998) is most likely too low and rather lies around 4 if we consider HyPy as close to the real PyC quantity as possible.

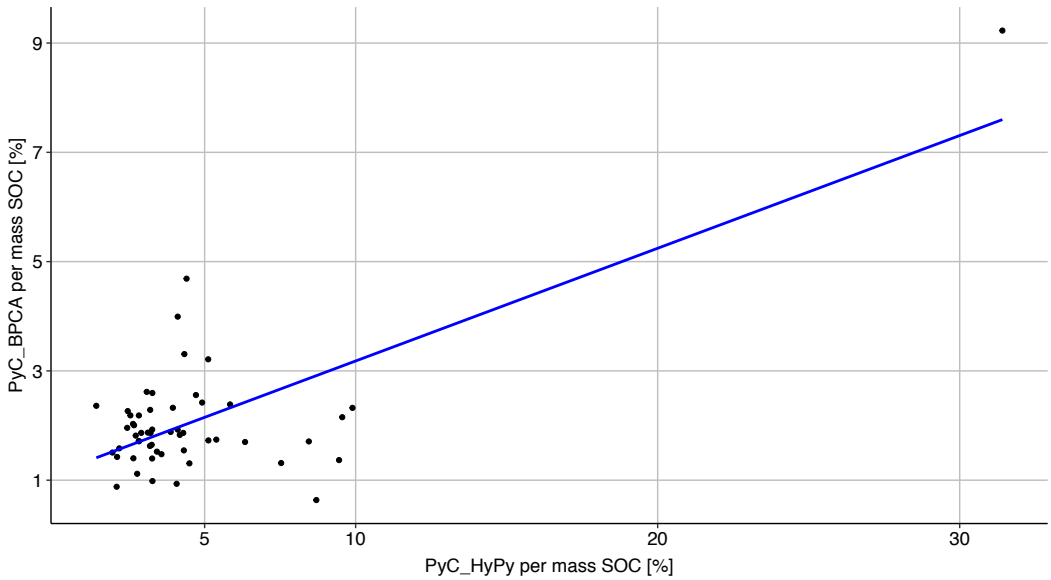


Figure S1: Relation between measured HyPy and BPCA PyC. The blue line is a linear regression line of the same with R^2 = 0.5 and p < 0.001.

Extended selection of study sites – Adopted with permission from González-Dominguez et al. (in rev.)

We followed a stepwise procedure (Figure S 2) to select the 54 study sites so that the effects 4 of biogeographic region, site temperature, site moisture, and the aggregated soil properties 5 and landform-related variables (PCo1, PCo2) were near-orthogonal (Figure S 3). A common limitation of studies on the drivers of SOC dynamics is the co-variation of controls in time and/or space, that makes challenging to partition their relative influences (Ciais et al., 2005; Wu et al., 2011). For example, if we take a set of random samples it would be very difficult to statistically distinguish between the effect of decreasing temperature and increasing moisture, as colder sites also tend to be moister. The knowledge-driven selection of study sites for soil research is not new (Addiscott and Wagenet, 1985), but its application is still far from common practice. In this work, we developed a statistics-based strategy to select, from the soil database of the Swiss Federal Institute for Forest, Snow and Landscape Research (WSL) (Walthert et al., 2013), a set of 54 sites spread over Switzerland with minimised co-variation of the putative drivers (i.e. maximising orthogonality/statistical independence). In this way, when applying multiple linear regression models summarized by analysis of variance, we can detect dynamics (i.e. middle points) and trends (i.e. 'extreme' points) in the relationships between SOC dynamics and drivers. The main hypothesis of this study is that site's temperature and moisture play a primary role on SOC dynamics, followed by soil properties and landform, accordingly the stepwise implementation of the selection strategy was performed as follows. For the selection we used the R software (version 3.3.2) (R Core Team, 2016):

1. **Definition of the exhaustive population within the study area.** By May 2014, the WSL database contained data on 1,050 profiles covering the main biogeoregions (i.e. Jura, Midland, Pre-Alps, Alps and Southern Alps) (Gonseth et al., 2001) and a vast range of climatic conditions. A 3% of the sites in the database belonged to the Long-term Forest Ecosystem Research Programme (LWF, German acronym). LWF sites are of special interest due to the intensive research activity and availability of data. Soil erosion and deposition are ubiquitous processes that play a major role on the redistribution and cycling of SOC at regional scales (Berhe et al., 2007). Studies conducted in forested areas have shown that strong topographic gradients are an important control of erosion and deposition patterns

(McCorkle et al., 2016; Stacy et al., 2015). For this reason, to assume that systems are near equilibrium (i.e. inputs ~ outputs) and that C losses due to erosion are negligible relative to the rate of SOC mineralisation, we excluded sites, excepting LWF sites, with slopes larger than 50% (26.57 degrees). Once we applied this filter, the working database counted 709 entries.

2. **Selection of the putative drivers.** To represent climate we included site's temperature (1981-2010 average mean monthly temperature) and moisture (1981-2010 dryness index). The dryness index is a proxy to soil moisture status based on the cumulative number of dry months. A dry month is one where the precipitation of the month is smaller than its potential evapotranspiration (Penman) (Slessarev et al., 2016). For soil properties and landform, we reduced the pH value, clay content (%), slope (%) and orientation (N-E-S-W) to two orthogonal variables (PCo1, PCo2) by principal coordinates analysis(Gower, 1966; Quinn and Keough, 2002). For the sites selection all data was sourced from the WSL database.
3. **Partition of the population into four equiprobable categories based on main hypothesized drivers.** As we hypothesise that climate plays a primary role on SOC dynamics, we partitioned the population into four equiprobable categories based on the median value of site temperature and moisture
4. **Spatial distribution of the population based on biogeographical regions**. Swiss biogeographical regions are the product of a statistical classification based on floristic and faunal distribution patterns (Gonseth et al., 2001), thus they are also connected to geophysical characteristics. To ensure the spatial distribution of the study sites, we subdivided each climatic treatment upon biogeographical regions. Some combinations of climate-biogeographical region did not occur or were under-represented. For example, we did not find moist and warm sites in the Alpine region, neither moist sites in the Southern Alps region.
5. **Partition of population into four categories based on secondary hypothesised drivers and non-automated selection of sites.** We reduced pH, clay (%), slope (%) and orientation (N-E-S-W) into two variables (PCo1 and PCo2) product of a principal coordinates analysis performed on the population dataset (PCoA; also known as classical or metric multidimensional scaling) (Gower, 1966; Quinn and Keough, 2002). PCoA is

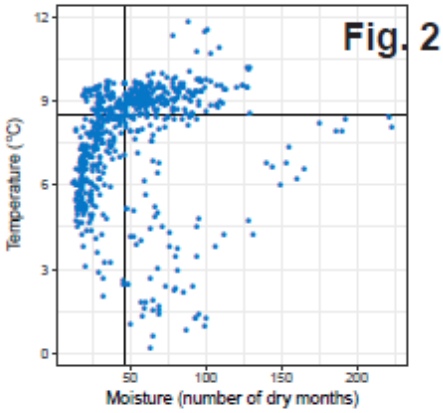
an ordination method that attempts to position objects in an Euclidean space of reduced dimensionality, while preserving their distance relationships of dissimilarity (or similarity) (Gower, 1966). As a result, in the graphical representation of the Euclidean space, the further sites plot to each other, the more dissimilar they are and vice-versa.

6. **Selection of study sites from two-dimensional Euclidean spaces defined by PCo1 and PCo2.** To select the 54 sites we position the data from each climate-biogeographical region combination into two-dimensional Euclidean spaces defined by pco1 and pco2. From here, we selected equidistant sites from the origin of coordinates. Due to missing points, some combinations were not sampled. These gaps are expected to have only minor influence on the regression analyses because they are spread rather than clustered over the full range of potential combinations.

Definition of the exhaustive population within the study area
Pre-processed soil database, N = 709. Fig. 1

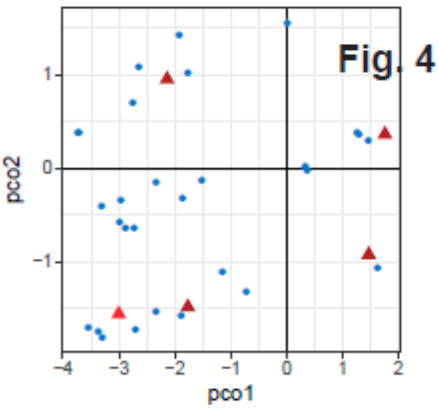
Definition of the putative drivers of SOC dynamics
Climate, soil properties & landform

Partition of the population into four equiprobable categories based on main putatitive drivers (i.e. site's temperature & moisture)
Fig. 2



Spatial distribution of the population based on biogeographical regions
Fig. 3

Partition of population into four categories based on secondary putative drivers
PCo axes are product of reducing the secondary putative drivers (i.e. pH, clay, slope degree and orientation) with principal coordinates analysis performed on the population dataset. Fig. 4



Non-automated selection of study sites from two-dimensional Euclidean spaces defined by PCo1 and PCo2
Sites selected, n = 54. Fig. 4 & 5

Figure S2 – Schematic representation of the stepwise statistics-based selection of the 54 study sites

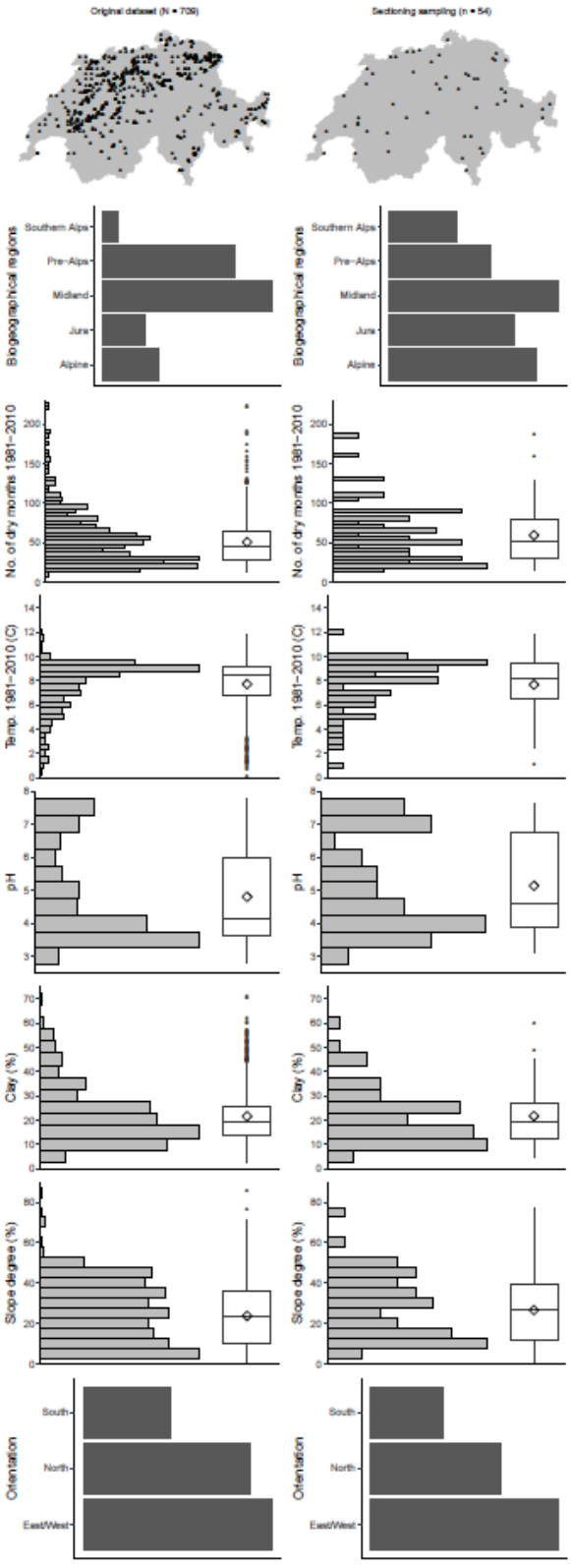


Figure S3 – Distribution of drivers' data between the forest soils database of the Swiss Federal Institute for Snow, Forest and Landscape Research (WSL) and the selected 54 study sites selected (n = 54). From the WSL database, sites with slopes > 50%, excepting those part of the Long-term Forest Ecosystem Research Programme sites, have been excluded (N = 709). All data sourced from the WSL database.

References

Addiscott, T.M., Wagenet, R.J., 1985. A Simple Method for Combining Soil Properties that Show Variability. Soil Sci. Soc. Am. J. 49, 1365. doi:10.2136/sssaj1985.03615995004900060007x

Ciais, P., Reichstein, M., Viovy, N., Granier, A., Ogée, J., Allard, V., Aubinet, M., Buchmann, N., Bernhofer, C., Carrara, A., Chevallier, F., De Noblet, N., Friend, a D., Friedlingstein, P., Grünwald, T., Heinesch, B., Keronen, P., Knohl, A., Krinner, G., Loustau, D., Manca, G., Matteucci, G., Miglietta, F., Ourcival, J.M., Papale, D., Pilegaard, K., Rambal, S., Seufert, G., Soussana, J.F., Sanz, M.J., Schulze, E.D., Vesala, T., Valentini, R., 2005. Europe-wide reduction in primary productivity caused by the heat and drought in 2003. Nature 437, 529–533. doi:10.1038/nature03972

Cotrufo, F.M., Boot, C., Abiven, S., Foster, E.J., Haddix, M., Reisser, M., Wurster, C.M., Bird, M.I., Schmidt, M.W.I., 2016. Quantification of pyrogenic carbon in the environment: An integration of analytical approaches. Org. Geochem. 100, 42–50. doi:10.1016/j.orggeochem.2016.07.007

Glaser, B., Haumaier, L., Guggenberger, G., Zech, W., 1998. Black carbon in soils : the use of benzenecarboxylic acids as specific markers. Org. Geochem. 29, 811–819.

Gower, J.C., 1966. Some distance properties of latent root and vector methods used in multivariate analysis. Biometrika 53, 325–338. doi:10.1093/biomet/53.3-4.325

Hammes, K., Schmidt, M.W.I., Smernik, R.J., Currie, L. a., Ball, W.P., Nguyen, T.H., Louchouarn, P., Houel, S., Gustafsson, Ö., Elmquist, M., Cornelissen, G., Skjemstad, J.O., Masiello, C. a., Song, J., Peng, P., Mitra, S., Dunn, J.C., Hatcher, P.G., Hockaday, W.C., Smith, D.M., Hartkopf-Fröder, C., Böhmer, A., Lüer, B., Huebert, B.J., Amelung, W., Brodowski, S., Huang, L., Zhang, W., Gschwend, P.M., Flores-Cervantes, D.X., Largeau, C., Rouzaud, J.-N., Rumpel, C., Guggenberger, G., Kaiser, K., Rodionov, A., Gonzalez-Vila, F.J., Gonzalez-Perez, J. a., de la Rosa, J.M., Manning, D. a. C., López-Capél, E., Ding, L., 2007. Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere. Global Biogeochem. Cycles 21. doi:10.1029/2006GB002914

Quinn, G.P., Keough, M.J., 2002. Experimental design and data analysis for

biologists, 1st ed. Cambridge University Press, New York.

R Core Team, 2016. R: A language and environment for statistical computing.

Slessarev, E.W., Lin, Y., Bingham, N.L., Johnson, J.E., Dai, Y., Schimel, J.P., Chadwick, O.A., 2016. Water balance creates a threshold in soil pH at the global scale. Nature 540, 567–569. doi:10.1038/nature20139

Walthert, L., Zimmermann, S., Walser, M., Jakob, P., Sutter, F., 2013. Forest-site ecology [WWW Document]. Swiss Fed. Inst. For. Snow Landsc. Res. Website.

Wu, Z., Dijkstra, P., Koch, G.W., Peñuelas, J., Hungate, B.A., 2011. Responses of terrestrial ecosystems to temperature and precipitation change: a meta-analysis of experimental manipulation. Glob. Chang. Biol. 17, 927–942. doi:10.1111/j.1365-2486.2010.02302.x

Statistical results

	BGR			TI			MI			TIxMI			pco1			pco2	
ANOVA configuration	Df	F value	P-value	Df	F value	P-value	Df	F value	P-value	Df	F value	P-value	Df	F value	P-value	Df	F value	P-value
HyPy ~ BGR + TIxMI + pco1 + pco2	4	0.67	0.613	1	0.31	0.579	1	6.91	0.012	1	1.28	0.264	1	5.5	0.024	1	3.06	0.087
BPCA ~ BGR + TIxMI + pco1 + pco2	4	1.07	0.38	1	0.06	0.8	1	0.64	0.43	1	1.13	0.29	1	1.51	0.23	1	0.16	0.69

	1. position			2. position			3. position			4. position			5. position			6. position	
HyPy and pH	Df	F value	P-value	Df	F value	P-value	Df	F value	P-value	Df	F value	P-value	Df	F value	P-value	Df	F value	P-value
HyPy ~ BGR + TIxMI + clay + **pH** + slope + orientation	1	10.43	0.003	1	10.91	0.002	1	7.28	0.01	1	5.24	0.03	1	4.82	0.04	1	3.82	0.058

	1. position			2. position			3. position			4. position			5. position			6. position	
BPCA and clay content	Df	F value	P-value	Df	F value	P-value	Df	F value	P-value	Df	F value	P-value	Df	F value	P-value	Df	F value	P-value
BPCA ~ BGR + TIxMI + **clay** + pH + slope + orientation	1	3.76	0.06	1	8.15	0.007	1	7.49	0.01	1	10.62	0.002	1	9.79	0.004	1	11.21	0.002

Abbreviations

HyPy	PyC content in SOC measured with the HyPy method, log-transformed
BPCA	PyC content in SOC measured with the BPCA method
BGR	Biogreographical region
TIxMI	Binary temperature index + binary moisture index and the interaction thereof
pco1	principal coordinate 1, including pH and clay content [%]
pco2	principal coordinate 2, including slope [%] and orientation [N, E, S, W]
clay	clay content [%]

Manuscript 3

Quantification of pyrogenic carbon in the environment: An integration of analytical approaches.

M. Francesca Cotrufo[1,2*], Claudia Boot[1,3], Samuel Abiven[4], Erika J. Foster[1,2], Michelle Haddix[1], Moritz Reisser[4], Christopher M. Wurster[5], Michael I. Bird[5] and Michael W. I. Schmidt[4]

1-Natural Resources Ecology Laboratory, Colorado State University, Fort Collins, Colorado

2-Department of Soil and Crop Sciences, Colorado State University, Fort Collins, Colorado

3-Department of Chemistry, Colorado State University, Fort Collins, Colorado

4-Soil Science and Biogeography Unit, University of Zurich, Zurich, Switzerland

5-College of Science, Technology and Engineering and Center for Tropical Environmental and Sustainability Science, James Cook University, Cairns, Queensland, Australia

+Corresponding Author: Francesca.cotrufo@colostate.edu

Contribution: MR measured and analysed the samples with DRIFT. MR contributed to the final version oft he manuscript. (No comprehensive author contributions given)

Published: Organic Geochemistry, July 2016
doi: 10.1016/j.orggeochem.2016.07.007

Keywords: pyrogenic carbon, black carbon, benzene polycarboxylic acids, hydrogen pyrolysis, mid infrared spectroscopy, fire, sediments, soils

Abstract

Pyrogenic Carbon (PyC), the product of incomplete combustion of biomass during fire, is now recognized as a significant component of the global carbon cycle. However, quantitative determination of PyC is challenging, in particular at large scale. We conducted a comparison of three methods for PyC analyses: Benzene Poly-Carboxylic Acid (BPCA) method, hydrogen pyrolysis (hypy) and Mid Infrared Spectroscopy (MIR) to identify a suitable approach for the determination of PyC at large geographical scales and across different environmental matrices. We analyzed samples (n=165) derived from a variety of matrices (i.e., forest floor, soils, sediments, and char), most of which were collected in the natural environment after fire. BPCA and hypy PyC estimates were linearly correlated (R^2 ranged between 0.74 and 0.92), thus suggesting that they can be merged in larger scale PyC syntheses. However, the slope of the regression varied among different matrices, ranging between 0.1 and 0.44, likely due to differences in the degree of aromatic condensation. MIR coupled with Partial Least-Squares Regression (MIR-PLSR) was demonstrated to be a very powerful tool to estimate PyC across a variety of environmental matrices, with high throughput and low analytical costs in comparison to the other two PyC analytical methods. Furthermore, we obtained accurate calibrations for MIR-PLSR by the hypy and the BPCA method, the latter in particular for soil samples. We, thus, conclude that reliable PyC estimates at large geographical scales and across different environmental matrices can be obtained by MIR-PLSR, previous calibration with hypy or BPCA, for matrices for which the BPCA PyC yields are known.

1. Introduction

Pyrogenic carbon (PyC) is produced by inefficient combustion of organic matter during fire, when up to 25% of the total carbon (C) available for combustion is converted to PyC (Santin et al., 2015). Globally, fires are estimated to generate between 114 and 379 Tg PyC per year, corresponding to approximately 0.2-0.6% of the annual terrestrial net primary production (Santin et al., 2016). In a recent estimate of the global PyC cycle, soils were recognized as a major PyC pool, ranging between 54-109 Pg (Bird et al., 2015). PyC is a ubiquitous component of soils, comprising up to 50% of the soil organic C (SOC), particularly prevalent in systems highly prone to fires (Schmidt et al., 1999; Skjemstad et al., 2002; Hammes et al., 2007; Cusack et al., 2012). From the soil, PyC can be transported and effectively stored in an "intermediate" sediment pool, before being delivered through rivers to the marine environment where the largest and longest term storage pool for PyC exists (Bird et al., 2015).

Despite its recognized importance, PyC is currently not explicitly considered as a C pool in the global carbon cycle, as published in the latest IPCC report (Stocker et al., 2014). Furthermore, PyC is not explicitly considered in current ecosystem C models and, at best, is treated as part of a larger "passive" C pool (Lehmann et al., 2008). With fire intensity and frequency predicted to increase due to climate and land use change (Liu and Wimberly, 2016), reliable measurements of PyC at global scale are necessary to better constrain global estimates of PyC pools and fluxes (Bird et al., 2015), and to incorporate them into global C models to accurately simulate biogeochemical C cycling under climate change scenarios.

While our mechanistic understanding of PyC dynamics in the soils and its movement via dissolution into rivers and the ocean is rapidly advancing (Abiven et al., 2011; Dittmar et al., 2012; Jaffe et al., 2013; Rumpel et al., 2015), our ability to produce large-scale PyC estimates for eventual parameterization and validation of models is still limited. There is, in fact, a need to identify economically viable, high throughput analytical approaches, possibly combining different techniques. Yet, before merging PyC data obtained using different techniques, it is important to recognize the different operationally defined analytical windows within the PyC continuum detected by each method, as emphasized by Hammes *et al.* [2007].

The BPCA method (Glaser et al., 1998; Brodowski et al., 2005) is currently used for PyC estimates in terrestrial and aquatic systems (Glaser and Amelung, 2003;

Schneider et al., 2011a; Jaffe et al., 2013; Wiedemeier et al., 2013; Boot et al., 2015). This technique has yielded data for deep soil horizons, and on a variety of other matrices (*e.g.*, fresh and aged charcoal, soils and fire residues; Hammes et al. (2008); Abiven et al. (2011); Eckmeier et al. (2013)). In addition, the BPCA method provides information about the aromaticity and condensation of the molecular clusters composing the PyC (Wiedemeier et al., 2015). However, BPCAs are only molecular markers of PyC and estimating total amounts of PyC from BPCA analyses is not straightforward. Based on stoichiometric calculations, PyC yields from the BPCA extraction method depends on degree of condensation, with a theoretical maximum yield of 67% for a fully condensed structure, and of 83% for a polyacene structure with all rings sharing two C atoms (Schneider et al., 2011b). Published C yields from BPCA analyses are 26 ±7% in marine systems (Ziolkowski et al., 2011) and 25.7 % in charred wood (Glaser et al., 1998). Based on these yield estimates, the BPCA values are often corrected by a factor of 0.27 when used for quantification (Glaser et al., 1998), yet a thorough investigation of PyC yields from the BPCA across different environmental matrices is missing. We refer here to PyC extracted by the BPCA method as $PyC_{BPCA.}$

Hydrogen pyrolysis (hypy) presents as a quantitative approach to the determination of PyC (Ascough et al., 2009; Meredith et al., 2012; Wurster et al., 2012; Wurster et al., 2013), with the potential to be used for the calibration of other less quantitative analytical approaches, such as BPCA. Hydrogen pyrolysis is a relatively new method which uses pyrolysis at a slow heating rate (8˚C per minute to 550˚C), coupled with high hydrogen pressures (>150bar) with a dispersed sulfide molybdenum catalyst. It separates labile C from stable polycyclic aromatic compounds, with an average ring cluster size >7, which we here refer to as PyC_{hypy}. PyC_{hypy} abundance is determined from the C content of the sample by elemental analysis following the hydropyrolytic reduction of labile C. Meredith et al. (2012) shown that conversions of ~ 100% are achieved for thermally labile materials, with the principal output being dichloromethane-soluble oil. They reported data on the performance of hypy for PyC measurement using all of the ring trial samples examined by Hammes et al. (2007). The study found that (i) all interfering materials were successfully removed by hypy with the exception of high rank coal, which is similar in composition to PyC, (ii) that for all sample matrices, including soils, the hypy results were well within the range of results reported by other techniques and that (iii) the analyses are highly reproducible (at ±0.5% CV or better).

Both BPCA and hypy require sample pre-processing and have a low sample throughput, reducing the feasibility of applying these methods for continental to global scale investigations. A more efficient, non-destructive and cost effective method that enables larger-scale PyC studies is Mid-Infrared spectroscopy (MIR). MIR has been used to characterize PyC particles for decades (Wood, 1988) and more recently to predict its content in soil (Bornemann et al., 2008). This technique is based on the fundamental molecular vibrations of soil components occurring in the MIR (between wavelengths of 2500- 25000 nm, i.e., 4000- 400 cm^{-1}). The position and the intensity of the signal can then be analyzed by integrating peaks of special interest (for example, several peaks of the MIR spectrum are related to aromatic functions, one of the major PyC material chemical structure) or by applying multivariate statistical techniques such as Partial Least-Squares Regression (PLSR) methods to relate one soil component or property to the MIR spectra. MIR coupled with PLSR has been widely used for the determination of various soil properties (Viscarra Rossel et al., 2006). However, quantification by MIR-PLSR requires a comparison to another quantitative method (Jauss et al., 2015). We refer here to the PyC MIR_PLSR estimates as $PyC_{MIR.}$

The overall goal of our study is to identify a feasible approach for the determination of PyC at large geographical scales, potentially involving many samples from different environmental matrices. Specifically, we aim to address the following questions: (1) Is there a relationship between the PyC_{hypy} and PyC_{BPCA} estimates, that can be used to quantify PyC yields from BPCA analysis, and allow merging PyC data from studies using hypy and BPCA? (2) Are there specific MIR features that correlate to the PyC_{hypy} and PyC_{BPCA} estimates? And then, (3) Can correlations between PyC_{hypy} and/or PyC_{BPCA} and MIR spectra be used to calibrate the MIR-PLSR, so that the latter can be used for large-scale PyC pool quantification? To address these questions we analyzed 165 samples from a variety of matrices (i.e., forest floor, soils, sediments, and char), the majority of which were collected in different forests and grassland sites after wild or managed fire, by the BPCA and the MIR-PLSR methods, and a subset (88) of those also by hypy (Table 1). We then assessed the degree of correspondence between the PyC estimates by the different methods. Most previous methods comparisons have been carried out on laboratory-produced chars, or on a few matrix standards (Hammes et al., 2007).

2. Material and methods

2.1 Sample description

The samples (n=165) used for this study are from a variety of matrices (Table 1). Forest floor samples (n=35) are the partially charred litter plus O horizon material from a coniferous (*Pinus ponderosa*) forest in the Cache la Poudre (CLP) watershed northwest of Fort Collins, CO, USA that experienced a variable severity wildfire in 2012 (Boot et al., 2015). Soil samples (total n=78) consist of the mineral soils from 0-5 and 5-15 cm depths (n=70) from the same CLP forest sites. Forest floor and soil sampling details can be found in Boot et al. (2015). The rest of the soil samples were from the Konza Prairie Biological Station from historically and annually burned grassland sites (n=8), and a full description of the sites and sampling is provided in Soong and Cotrufo (2015).

Table 1. Summary of samples numbers stratified by substrate and method of analysis.

Substrate	Subtype	BPCA	MIR	hypy
Mineral soil	**total**	**78**	**78**	**43**
	grassland	8	8	8
	coniferous	70	70	35
Forest floor	coniferous	**35**	**35**	**17**
Char		**5**	**5**	**5**
Fire layer		**8**	**8**	**6**
Sediment bank	**total**	**18**	**18**	**17**
	coarse plant	9	9	9
	dark mineral	3	3	3
	light mineral	4	4	4
	sand	2	2	1
Sediment fence		**21**	**21**	**0**
grand total		**165**	**165**	**88**

River bank sediment samples (total n=18) originated from sediment bank cores collected along the CLP river in 2012. Cores were partitioned into visibly discreet layers made up of coarse organic material (n=9), light mineral sediments (n=4), dark mineral sediment (n=3), and sand (n=2). Sampled river bank locations varied in length from 9 m to 60 m. At each bank a grid was set up to randomly locate sampling cores.

Figure 1: Images of 5 of 8 'fire layer' samples collected in the Cache la Poudre watershed, the additional 3 fire layer samples were not photographed. A. PyC fire layer 1 ~0.05 m depth, PyC_{hypy} = 15.6, PyC_{BPCA} = 3.93 g kg^{-1} dry mass. B. PyC fire layer 1 ~0.9 m depth, PyC_{hypy} = 4.31, PyC_{BPCA} = 1.57 g kg^{-1} dry mass. C. PyC fire layer 2 ~0.5 m depth, PyC_{hypy} = 25.3, PyC_{BPCA} = 12.0 g kg^{-1} dry mass. D. PyC fire layer 3 ~1.1 m depth, PyC_{hypy} = 10.4, BC_{BPCA} = 3.59 g kg^{-1} dry mass. E. PyC fire layer 4 ~0.63 m depth, PyC_{hypy} = 3.74, PyC_{BPCA} = 0.57 g kg^{-1} dry mass.

Grid cells varied from 0.5 m to 5 m depending on the length of the bank, and two to five grid cells were randomly sampled from each of the four quadrants: upstream, downstream, towards the river, towards the land. A 5.4 cm inner diameter core fitted with a plastic sleeve was used to sample the cores and keep cores intact until further processing in the lab. The depth of the sediment banks varied and cores were taken down to 30 cm. Cores were stored at 4°C until processing, which included slicing cores by hand into coarse organic, dark mineral, and light mineral layers. Total weight of the core and each component was recorded. Components were air-dried, sieved through a 2 mm mesh screen with rocks removed and weighed. Component dry weights were corrected for rocks. A subsample was taken from each sample component, finely ground, and oven-dried at 105°C prior, for dry weight correction and subsequent analyses.

Chars (n=5) were derived from two different feedstocks and pyrolysis conditions. One char sample derives from virgin pine wood pyrolyzed at a temperature range from 400-700°C with less than 5 minutes in reaction (Biochar Solutions Inc.). The second

char was produced by slow pyrolysis at 450°C of pine beetle killed wood (Biochar Now, Inc.). This was analyzed as pure char, as well as ground to a fine texture and mixed with soil at a rate of 5, 20 and 50% soil weight (n=3).

Fire layers (n=8) were collected from the CLP watershed. Areas of side channel banks, scoured during the September 2012 flooding revealed layers of dark sediment at various depths within the soil profile from just below the surface to 1.1 m depth (Figure 1). Using a knife or trowel, material from within the layer was scraped into a plastic bag, transported to the lab and stored at -10 °C. They were finely ground and oven-dried prior to analyses.

Terrestrial sediment fence samples (n=21) were from sediment fences established in the CLP watershed in fall 2012, constructed similarly to Robichaud and Brown (2002) and described in Schmeer (2014) . Sediments were collected between August 2012 and September 2013 from the fences following rainfall events, that mobilized sediment by overland flow. These samples were also finely ground and oven dried prior to analysis.

2.2 PyC analyses

a. Benzene Poly Carboxylic Acids

BPCA analysis for PyC determination was conducted on all samples using high performance liquid chromatography (HPLC) equipped with a photo diode array detector as described previously (Wiedemeier et al., 2013). Briefly, 50- 150 mg of finely ground sample was oxidized in nitric acid, purified with cation exchange resin, concentrated and analyzed via HPLC using a five-point calibration of BPCA standards (Boot et al., 2015). We used values on a per mass basis to compare among methods. This eliminates additional error that could arise from measuring C content in charred soils. We also calculated the ratio between B6 and total BPCA and used it as an indicator of condensation. The B6CA represents the most condensed moieties of the char graphitic structure as represented by the BPCA method. The ratio B6 to total BPCA has been used to show the degree of condensation in charcoal samples (Schneider et al., 2011a; Wiedemeier et al., 2015).

b. Hydrogen pyrolysis (hypy)

Previous work developed the hypy method to quantify stable polycyclic aromatic carbon of ring cluster size greater than ca. 7 (coronene)(Love et al., 1995; Ascough et al., 2009; Meredith et al., 2012; Wurster et al., 2012; McBeath et al., 2015). Briefly, a subset of samples (n=88; Table 1) were loaded with a dispersed sulphide

molybdenum (Mo) catalyst to equal ~1% of sample total organic C (TOC). Low C samples (<10% TOC) and high C samples (>10% TOC) were mixed with 5% or 10% Mo catalyst by weight using an aqueous/methanol solution of ammonium dioxy-dithiomolybdate [$(NH_4)_2MoO_2S_2$]. Catalyst loaded samples were placed in an ultrasonic bath to help dissolution, evaporated at 70°C on a heating block and dried at 60°C prior to analysis. Samples were placed, two at a time, into the reactor of the hypy rig (Strata Technology Ltd., Middlesex, UK), pressurized with 150 bar of hydrogen with a sweep gas flow of 5 L min^{-1} (measured at ambient temperature and pressure) to remove pyrolysis products from the vessel. A pre-programmed temperature profile heated the samples from 50°C to 250°C at 300°C min^{-1}, then from 250°C to 550°C at 8°C min^{-1}, holding at the final temperature for 2 min. Weight loss was recorded. PyC was determined by mass balance involving comparison of carbon content and sample mass before and after hydrogen pyrolysis adjusted. Values were corrected for catalyst content and PyC formed during analysis as described in Wurster et al. (2012). Carbon content was determined by elemental analysis using a LECO CNS2000 carbon analyzer (LECO Corporation, St Joseph, MI)

c. MIR spectroscopy

Mid-infrared spectra were acquired by diffuse reflectance infra-red Fourier transform spectroscopy (DRIFT). The samples were homogenized in an Eppendorf tube at a frequency of 25 cm^{-1} for 3 min. Prior to measurement, the samples were oven dried at 70°C. Spectra were recorded using a Bruker TENSOR 27 spectrophotometer (Fällanden, Switzerland) from 4000–400 cm^{-1} (average of 64 scans per sample at 4 cm^{-1} resolution). A KBr reference background spectrum was recorded at the start of the scanning session and every 25 samples during each session. KBr is a non-absorbing material to mid infra-red and was used as a background to correct for the eventual changes in atmospheric conditions (water and CO_2 mainly). Additionally, the chernozem soil sample from the ring trial (Hammes et al., 2007) was also used every 25^{th} sample to check for internal drift. We observed no changes in the spectrum of this internal standard during the analysis. Assignments of the infrared absorption bands were based on a literature compilation (Guo and Bustin, 1998; Moore and Owen, 2001; Baldock and Smernik, 2002; Weiland and Guyonnet, 2003; Nuopponen et al., 2006).

2.3 Data analyses

The relationships between PyC_{BPCA} and PyC_{hypy} data were evaluated using linear models in order to compare slopes across the different environmental matrices using the SAS Proc Mixed model grouped by biologically distinct groups of: char, fire layer, forest floor, soil and river bank sediment. Data were checked for normality and equal variance, and analysis of covariance (ANCOVA) with post-hoc pairwise Tukey's HSD comparisons was used to compare slopes and the ratio of B6 over total BPCAs among groups. Statistical analyses were conducted in SAS 9.4.

Multivariate calibrations using PLSR were performed on baseline corrected MIR spectra using the R 'pls' package (Mevik et al., 2011). We focused on the 2500-400 cm^{-1} of the spectra as this range contained most of the information related to the organic associated chemical functionalities, in particular the charcoal relevant aromatic related structures of the relevant information for PyC (Chatterjee et al., 2012). In addition, this part of the spectrum only contains few mineral associated functionalities, and so its selection minimized the potential analytical noise created by inorganic material. Leave-one-out cross validation was used to select the optimal number of factors to be used in the calibration models. Five components were used as the optimal number of PLSR factors, following the principle of parsimony, i.e., the lowest number of factors representing the highest explanatory power of analysis. The calibration between PyC_{MIR} and PyC_{BPCA} / PyC_{hypy} was completed for all the samples together and for the different matrices separately.

3. Results

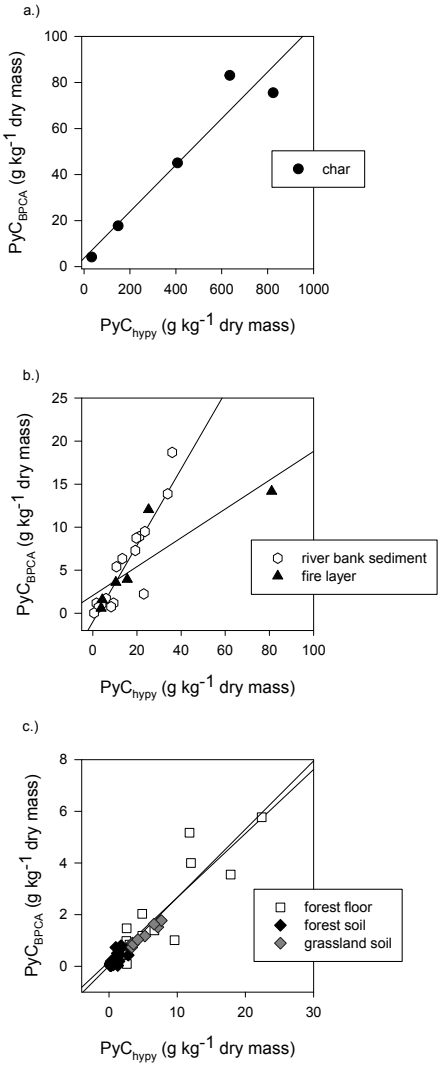
3.1 Relationship between PyC_{hypy} and PyC_{BPCA}.

PyC_{hypy} values were always greater than PyC_{BPCA}. The latter ranged from 0.02 to 83.07 g kg^{-1} dry mass, while PyC_{hypy} ranged from 0.15 to 824.2 g kg^{-1} dry mass. The relationship between PyC_{hypy} and PyC_{BPCA} measurements differed among substrate types (Figure 2, Table 2). Chars had the largest difference with PyC_{BPCA} amounts, approximately 10% of PyC_{hypy} values (Figure 2a), river sediment banks exhibited the smallest difference with $PyC_{hypy,}$ approximately double PyC_{BPCA} amounts (Figure 2b). Intermediate values were found for fire layers (Figure 2b), and forest floor and soils (Figure 2c). Pairwise comparison of slopes indicated that char and fire layers were not significantly different from each other; fire layer, forest floor and soils were not significantly different; and river sediment banks were significantly different to all other substrate types (Table 2).

Table 2. Summary of regression statistics for comparison among the different matrices.

Matrices	n	linear fit	R^2	adj R^2	p value*	pair-wise
char	5	$PyC_{BPCA} = 3.66 + 0.10 * PyC_{hypy}$	0.92	0.90	0.0094	a
fire layer	6	$PyC_{BPCA} = 2.06 + 0.17 * PyC_{hypy}$	0.74	0.68	0.0272	ab
forest floor	14	$PyC_{BPCA} = 0.18 + 0.25 * PyC_{hypy}$	0.76	0.74	<0.001	b
soil	41	$PyC_{BPCA} = 0.05 + 0.23 * PyC_{hypy}$	0.89	0.89	<0.001	b
sediment bank	16	$PyC_{BPCA} = -0.99 + 0.44 * PyC_{hypy}$	0.82	0.81	<0.001	c

*Reported p values refer to the significance of fit. P values for intercepts were not significantly different from 0, and they were: char 0.697; fire layer 0.304; forest floor 0.660; river sediment bank 0.343; soil 0.133, so none that were significantly different from 0.



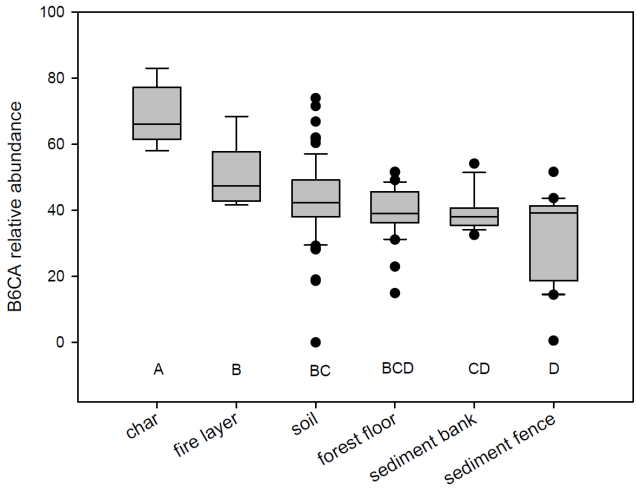


Figure 3: Box plot of the degree of aromatic condensation measured as the B6 relative abundance (i.e., B6/BPCA) for the different matrices. The number of observations of each matrix is reported in Table1. The post-hoc Tukeys test pairwise differences are indicated by the capital letters.

Figure 2: Relationships between the PyC determined by hydrogen pyrolysis (PyC_{hypy}) and the PyC measured by the benzene polycarboxylic acid method (PyC_{BPCA}) for (a) char, (b) sediment and fire layer, and (c) forest floor and soil samples. Equations and significance of regression lines are reported in Table 2.

Only the regressions for char and fire layer samples had appreciable positive intercepts (Table 2), although they were not statistically significant from zero (p=0.697 and p=0.304, respectively), possibly because of the low sample numbers. Char was also the matrix with the highest degree of condensation as estimated by the relative abundance of B6 over the total BPCAs (Figure 3). Across the five matrices, average values of degree of condensation were linearly and inversely related to the slope of PyC_{BPCA} *versus* PyC_{hypy} regression as reported in Table 2 (slope = 0.627 – 0.008(B6CA); R^2 = 0.71; p=0.075).

3.2 MIR-PLSR as a predictor for PyC_{BPCA} and PyC_{hypy}.

MIR-PLSR prediction quality varied across methods and matrices (Figure 4). Overall, the PyC_{hypy} values were better predicted than the PyC_{BPCA} values, in all matrices and despite the lower number of samples used in the model (Table 1). The PyC_{hypy} variance explained by the MIR-PLSR model was always above 85%, while variance explained for the PyC_{BPCA} was only above 85% for the soil samples. Among the different matrices, soil samples were the best predicted by the model, both for PyC_{hypy} and PyC_{BPCA}. However, soil samples were the most numerous (Table 1) and had the narrower value range (0-8 mg C. g^{-1} for PyC_{hypy} and 0- 2 mg C g^{-1} for PyC_{BPCA}). The prediction was poorer for sediments and forest floor, particularly for predictions with the PyC_{BPCA} method. For these matrices, the model tended to underestimate the higher PyC content values. The high values were also the reason for the relatively poor prediction of the PyC_{BPCA}, as compared to the PyC_{hypy}, when all the samples were analyzed together (Figure 4).

The contribution of the spectra regions (loading values) used to construct the predictive models, for the two main components of the PLSR, is reported in Figure 5. This provides an indication of which chemical features are used to predict PyC_{hypy} and PyC_{BPCA} values for the all samples model or for the individual matrices. The contributing peaks varied mainly across matrices. Peaks corresponding to cellulose (1260-1210 cm^{-1}) and lignin (1510-1500 cm^{-1}) played a more important role for forest floor and sediment samples prediction, while aromatic (1610-1570 cm^{-1} and 1430 – 1380 cm^{-1}) and aliphatic features (1060-1020 cm^{-1}) were central in the case of soil

samples. This would indicate that the prediction of PyC in forest floor and sediment samples is rather based on the uncharred part of the organic matter (prediction by default) since the char-related features in these samples were very similar.

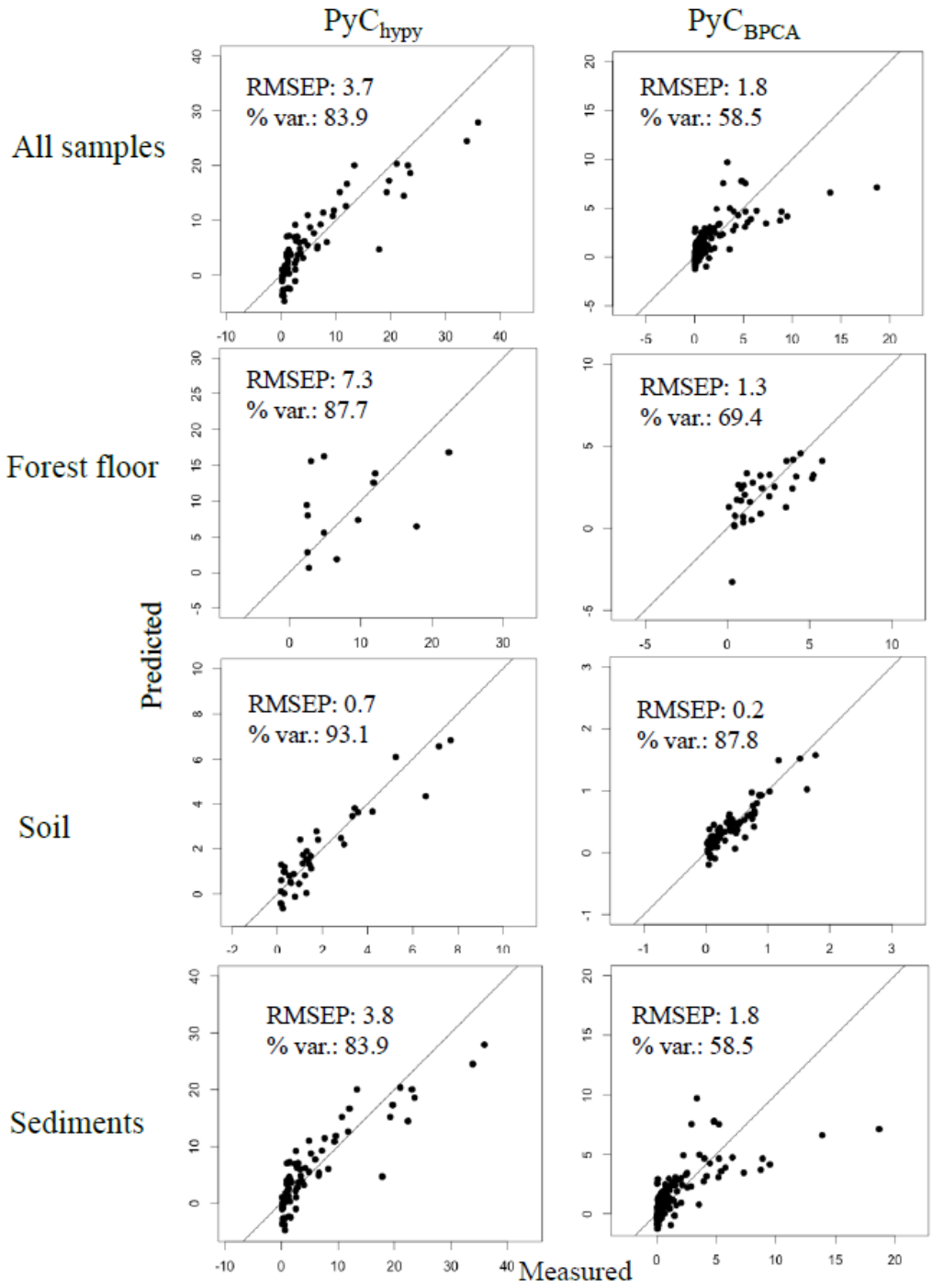


Figure 4: Relationships between the measured values of PyC_{hypy} and PyC_{BPCA} (g kg^{-1} dry mass) and those modelled by MIR-PLSR (PyC_{MID}), for all samples together or independently for forest floor, soil and sediment samples. Root Mean Square Error of Prediction (RMSEP) and % variance explained are reported for each regression.

The difference in spectra loading between the two methods was marginal, except for forest floor samples (Figure 5), but in this case only few samples were analyzed with

hypy (Table 1). When all the samples were considered together, the peaks involved in the construction of the predictive models for PyC_{hypy} and PyC_{BPCA} were very similar.

In all cases, the C-H bending deformation chemical features (880, 805, 745 cm^{-1}) were surprisingly never well represented in the models. Peaks at these three wavelengths are usually very specific to charcoal material.

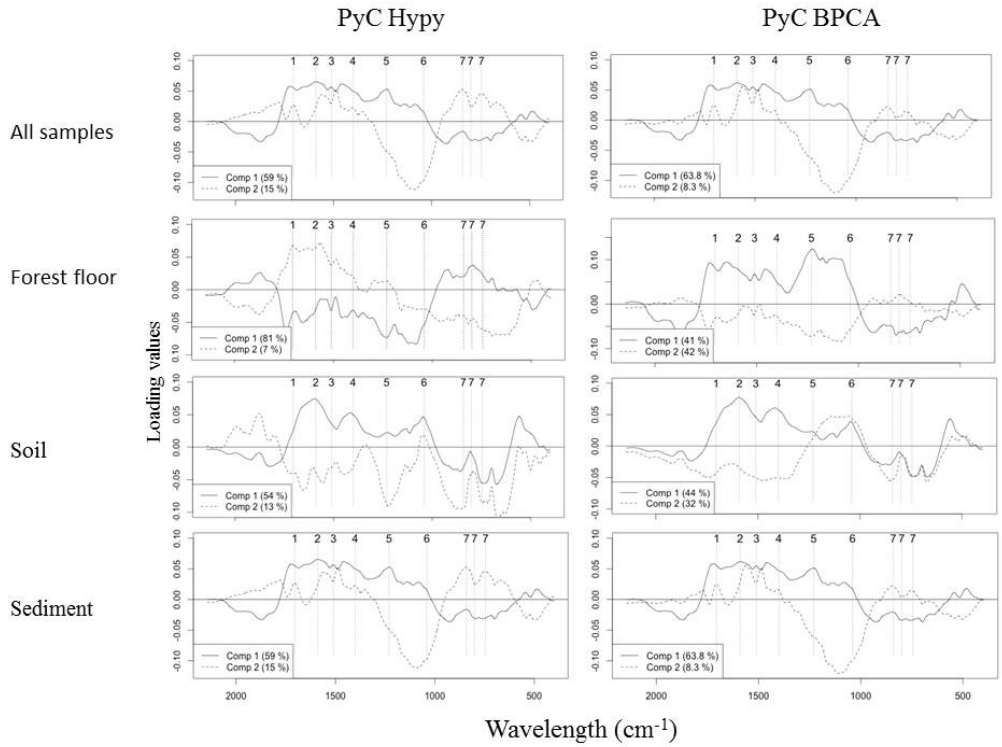


Figure 5: Contribution of the spectra regions (loading values) used to construct the predictive models in figure 4, for the two main components of the partial least-squares regressions. Numbers indicate major MIR adsorption bands (cm^{-1}), , with description and in brackets the prevailing trend with increasing PyC: 1 = 1730-1680, Aromatic carbonyl/carboxyl C=O stretch (increase); 2 = 1610-1570, C=C stretch (increase); 3 = 1510-1500, Lignin, aromatic C=C stretch (decrease); 4= 1430-1380, Aromatic C=C stretch (increase); 5= 1260-1210, Cellulose (decrease); 6= 1060-1020, Aliphatic C-O- and alcohol C-O stretch (decrease); 7 =880, 805, 745, C-H aromatic bending deformation (increase).

4. Discussion

The BPCA is currently among the most used technique for PyC determination at a variety of scale and in different matrices (Glaser and Amelung, 2003; Schneider et al., 2011a; Jaffe et al., 2013; Wiedemeier et al., 2013; Boot et al., 2015). More recently extensive PyC analyses have been conducted using hypy and these data will soon become available. However PyC data generated by those two methods cannot be directly merged since hypy is thought to yield approximately 100% of the

PyC with aromatic ring cluster size of >7 (Meredith et al., 2012; Wurster et al., 2013), while the BPCA method extracts PyC markers, and thus by definition yields less than 100% PyC, theoretically varying with level of aromatic condensation (Schneider et al., 2011b). A goal of this study was to compare PyC_{BPCA} and PyC_{hypy} values measured on a variety of matrices and identify controls on their relationship which would prove useful to merge data generated by those two approaches, as well as to use PyC_{BPCA} values in a global synthesis of PyC stocks.

In this study we proved that while significant positive correlations exist between PyC_{BPCA} and PyC_{hypy}, these varied significantly across the different matrices (Figure 2, Table 2). In particular char and fire layer samples exhibited the lowest PyC_{hypy}yield by the BPCA method (10 and 17%, respectively), as compared to the soil and sediment samples with yields of 23% and 44%, respectively (Table 2). The PyC in chars, derived from industrial pyrolysis, had a higher degree of aromatic condensation as compared to PyC in soils or sediments (Figure 3), derived from partially burned plant biomass during fires. These observations are consistent with the theoretical knowledge that PyC yields from the BPCA method decrease with increasing level of aromatic condensation (Schneider et al., 2011a), and that hypy quantifies peri-condensed aromatic clusters of >7 rings (Meredith et al., 2012) . Additionally, a positive, but non-significant, intercept was found in the PyC_{BPCA} *versus* PyC_{hypy} relationship for the char and fire layer samples (Table 2), indicating the potential for presence of PyC undetected by the BPCA method in these samples. Conversely, a negative, but non-significant, intercept was found for the sediment samples, which were largely comprised of light partially burned plant material. Our study supports the finding that hypy effectively measures highly condensed PyC, while removing the less aromatic, likely more labile, PyC structures (Wurster et al., 2013). These labile PyC structures are apparently more effectively analyzed by the BPCA method, although the PyC component removed by hypy could also be quantified, for example by HPLC.

In search for an inexpensive and reliable approach to determine PyC at broad scale, MIR PLRS models has been previously used to estimate PyC in soils, using either BPCA (Bornemann et al., 2008) or UV-NMR (Janik and Skjemstad, 1995; Janik et al., 2007; Jauss et al., 2015) for calibration. Here we demonstrated that PyC can be predicted by MIR-PLSR in a variety of matrices, beside soils, using PyC measured by both BPCA and hypy for calibration (Figure 3). However, PyC_{BPCA} was less well predicted, particularly for high values.

The peaks contributing to these predictions were surprisingly similar between methods, with both plant- and pyrogenic-related chemical functionalities included in the prediction (*e.g.*, cellulose, lignin and aromatics (Figure, 5). However, while PyC_{BPCA} was more specific to aromatic ring content, PyC_{hypy} included large molecules, possibly because the PyC content is also related to the total organic C content of the samples and part of the prediction for PyC may relate to the prediction for total organic C.

Across both methods, we found a better MIR-PLSR prediction for soil and sediments over char matrices, likely as a result of the MIR technical features. Pure PyC materials, like char, are usually difficult to analyze directly by MIR. This is because at high degrees of chemical condensation level, MIR wavelengths are absorbed and the resulting spectra are flat and noisy (Abiven, personal communication; Guo and Bustin, 1998). For more accurate analysis of highly condensed samples, in this study we used KBr as a neutral buffer to dilute the signal (Wood, 1988). In the case of sediment and soil samples, the mineral phase serves as a buffer, insuring a signal of higher quality. Also, the prediction of PyC somehow competes with the rest of the organic matter; thus with decreasing organic matter content, the accuracy of PyC prediction increases.

The similarity between forest floor and sediment samples model loading was surprising (Figure 5). We suspect it may be due to the larger PyC content in the forest floor and sediment samples as compared to the soil samples, where aromatic features are probably more specific to PyC. This similarity may also be due to undecomposed organic material in the forest floor and sediment samples, either freshly deposited on the soil surface or kept intact in the anoxic sediment environment.

In this study we demonstrated that estimates of PyC by the BPCA and the hypy methods are well correlated and thus can be merged in larger scale PyC synthesis work. However, conversion factors vary among different matrices, likely due to differences in the degree of aromatic condensation. MIR-PRLS is confirmed as a very powerful, cost effective tool to estimate PyC, not only in soils, but also across a variety of environmental matrices. Further, good calibrations can be obtained by both the hypy or BPCA methods, in particular for soil samples. While significant model calibrations were obtained with relatively low measured values, we suggest that future calibration should use relatively high sample numbers (i.e. 50 and higher), particularly for the BPCA method.

Acknowledgement

We would like to thank Tara Baker, Geoffrey Bedrosian, Jake Betzen, Bryan Brown, Joey E'Silva, Claire Freeman, Michael Jurich, Daniel Kovar, Robert Murphy, Halle Poppaw, and Allison Reser for forest floor, soil and sediment samples collection and processing. This work was supported by the US NSF-CNIC project # 1427557 and the US NSF-RAPID project # 1261383. We thank the two anonymous referees for the time and effort provided in the review.

The PyC used in this study is deposited in the Colorado State University digital repository and can be accessed at http://hdl.handle.net/10217/170584.

References

Abiven, S., Hengartner, P., Schneider, M.P.W., Singh, N., Schmidt, M.W.I., 2011. Pyrogenic carbon soluble fraction is larger and more aromatic in aged charcoal than in fresh charcoal. Soil Biology and Biochemistry 43, 1615-1617.

Ascough, P.L., Bird, M.I., Brock, F., Higham, T.F.G., Meredith, W., Snape, C.E., Vane, C.H., 2009. Hydropyrolysis as a new tool for radiocarbon pre-treatment and the quantification of black carbon. Quaternary Geochronology 4, 140-147.

Baldock, J.A., Smernik, R.J., 2002. Chemical composition and bioavailability of thermally, altered Pinus resinosa (Red Pine) wood. Organic Chemistry 33, 1093-1109.

Bird, M.I., Wynn, J.G., Saiz, G., Wurster, C.M., McBeath, A., 2015. The Pyrogenic Carbon Cycle. Annual Review of Earth and Planetary Sciences 43.

Boot, C.M., Haddix, M., Paustian, K., Cotrufo, M.F., 2015. Distribution of black carbon in ponderosa pine forest floor and soils following the High Park wildfire. Biogeoscience 12, 3029-3039.

Bornemann, L., Welp, G., Brodowski, S., Rodionov, A., Amelung, W., 2008. Rapid assessment of black carbon in soil organic matter using mid-infrared spectroscopy. Organic Geochemistry 39, 1537-1544.

Brodowski, S., Rodionov, A., Haumaier, L., Glaser, B., Amelung, W., 2005. Revised black carbon assessment using benzene polycarboxylic acids. Organic Geochemistry 36, 1299-1310.

Chatterjee, S., Santos, F., Abiven, S., Itin, B., Stark, R.E., Bird, J.A., 2012. Elucidating the chemical structure of pyrogenic organic matter by combining magnetic resonance, mid-infrared spectroscopy and mass spectrometry. Organic Chemistry 51, 35-44.

Cusack, D.F., Chadwick, O.A., Hockaday, W.C., Vitousek, P.M., 2012. Mineralogical controls on soil black carbon preservation. Global Biogeochemical Cycle 26.

Dittmar, T., de Rezende, C.E., Manecki, M., Niggemann, J., Ovalle, A.R.C., Stubbins, A., Bernardes, M.C., 2012. Continuous flux of dissolved black carbon from a vanished tropical forest biome. Nature Geoscience 5, 618-622.

Eckmeier, E., Mavris, C., Krebs, R., Pichler, B., Egli, M., 2013. Black carbon contributes to organic matter in young soils in the Morteratsch proglacial area (Switzerland). Biogeosciences 10, 1265-1274.

Glaser, B., Haumaier, L., Guggenberger, G., Zech, W., 1998. Black carbon in soils: the use of benzenecarboxylic acids as specific markers. Organic Geochemistry 29, 811-819.

Glaser, B., Amelung, W., 2003. Pyrogenic carbon in native grassland soils along a climosequence in North America. Global Biogeochemical Cycle 17.

Guo, Y., Bustin, R.M., 1998. FTIR spectroscopy and reflectance of modern charcoals and fungal decayed woods: implications for studies of inertinite in coals. International Journal of Coal Geology 37, 29-53.

Hammes, K., Schmidt, M.W.I., Smernik, R.J., Currie, L.A., Ball, W.P., Nguyen, T.H., Louchouarn, P., Houel, S., Gustafsson, O., Elmquist, M., Cornelissen, G., Skjemstad, J.O., Masiello, C.A., Song, J., Peng, P., Mitra, S., Dunn, J.C., Hatcher, P.G., Hockaday, W.C., Smith, D.M., Hartkopf-Froeder, C., Boehmer, A., Luer, B., Huebert, B.J., Amelung, W., Brodowski, S., Huang, L., Zhang, W., Gschwend, P.M., Flores-Cervantes, D.X., Largeau, C., Rouzaud, J.N., Rumpel, C., Guggenberger, G., Kaiser, K., Rodionov, A., Gonzalez-Vila, F.J., Gonzalez-Perez, J.A., de la Rosa, J.M., Manning, D.A.C., Lopez-Capel, E., Ding, L., 2007. Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere. Global Biogeochemical Cycle 21.

Hammes, K., Torn, M.S., Lapenas, A.G., Schmidt, M.W.I., 2008. Centennial black carbon turnover observed in a Russian steppe soil. Biogeosciences 5, 1339-1350.

Jaffe, R., Ding, Y., Niggemann, J., Vahatalo, A.V., Stubbins, A., Spencer, R.G.M., Campbell, J., Dittmar, T., 2013. Global Charcoal Mobilization from Soils via Dissolution and Riverine Transport to the Oceans. Science 340, 345-347.

Janik, L., Skjemstad, J., 1995. Characterization and analysis of soils using mid-infrared partial least-squares .2. Correlations with some laboratory data. Soil Research 33, 637-650.

Janik, L.J., Skjemstad, J.O., Shepherd, K.D., Spouncer, L.R., 2007. The prediction of soil carbon fractions using mid-infrared-partial least square analysis. Soil Research 45, 73-81.

Jauss, V., Johnson, M., Krull, E., Daub, M., Lehmann, J., 2015. Pyrogenic carbon controls across a soil catena in the Pacific Northwest. Catena 124, 53-59.

Lehmann, J., Skjemstad, J., Sohi, S., Carter, J., Barson, M., Falloon, P., Coleman, K., Woodbury, P., Krull, E., 2008. Australian climate-carbon cycle feedback reduced by soil black carbon. Nature geoscience 1, 832-835.

Liu, Z., Wimberly, M.C., 2016. Direct and indirect effects of climate change on projected future fire regimes in the western United States. Science of The Total Environment 542, 65-75.

Love, G.D., Snape, C.E., Carr, A.D., Houghton, R.C., 1995. Release of covalently-bound alkane biomarkers in high yields from kerogen via catalytic hydropyrolysis. Organic Geochemistry 23, 981-986.

McBeath, A.V., Wurster, C.M., Bird, M.I., 2015. Influence of feedstock properties and pyrolysis conditions on biochar carbon stability as determined by hydrogen pyrolysis. Biomass and Bioenergy 73, 155-173.

Meredith, W., Ascough, P.L., Bird, M.I., Large, D.J., Snape, C.E., Sun, Y., Tilston, E.L., 2012. Assessment of hydropyrolysis as a method for the quantification of black carbon using standard reference materials. Geochimica and Cosmochimica Acta 97, 131-147.

Mevik, B.H., R., W., K.H., L., 2011. Partial Least Squares and Principal Component regression, R Package, p. 56.

Moore, A.K., Owen, N.L., 2001. Infrared spectroscopic studies of solid wood. Applied Spectroscopy Reviews 36, 65-86.

Nuopponen, M.H., Birch, G.M., Sykes, R.J., Lee, S.J., Stewart, D., 2006. Estimation of wood density and chemical composition by means of diffuse reflectance midinfrared Fourier transform (DRIFT-MIR) spectroscopy. Journal of Agricultural and Food Chemistry 54, 34-40.

Robichaud, P.R., Brown, R.E., 2002. Silt fences: An economical technique for measuring hillslope soil erosion, Gen. Tech. Rep. U.S. Department of Agriculture, Forest Service, Rocky Mountain Research Station, Fort Collins, CO, p. 24.

Rumpel, C., Leifeld, J., Santin, C., Doerr, S., 2015. Movement of biochar in the environment. Biochar for Environmental Management: Science, Technology and Implementation (second edition). New York: Routledge, 283-298.

Santin, C., Doerr, S.H., Preston, C.M., Gonzalez-Rodriguez, G., 2015. Pyrogenic organic matter production from wildfires: a missing sink in the global carbon cycle. Glob. Change Biol. 21, 1621–1633.

Santin, C., Doerr, S.H., Kane, E., Masiello, C., Ohlson, M., de la Rosa, J.M., Preston, C.M., Dittmar, T., 2016. Towards a global assessment of pyrogenic carbon from vegetation fires. Global Change Biololy, 22,76-91.

Schmeer, S.R., 2014. Post-fire erosion response and recovery, High Park Fire Colorado, Department of Ecosystem Science and Sustainability. Colorado State University, Fort Collins, CO.

Schmidt, M.W.I., Skjemstad, J.O., Gehrt, E., Kogel-Knabner, I., 1999. Charred organic carbon in German chernozemic soils. European Journal of Soil Science 50, 351-365.

Schneider, M.P.W., Hilf, M., Vogt, U.F., Schmidt, M.W.I., 2011a. The benzene polycarboxylic acid (BPCA) pattern of wood pyrolyzed between 200 degrees C and 1000 degrees C. Organic Geochemistry 41, 1082-1088.

Schneider, M.P.W., Smittenberg, R.H., Dittmar, T., Schmidt, M.W.I., 2011b. Comparison of gas with liquid chromatography for the determination of benzenepolycarboxylic acids as molecular tracers of black carbon. Organic Geochemistry 42, 275-282.

Skjemstad, J.O., Reicosky, D.C., Wilts, A.R., McGowan, J.A., 2002. Charcoal carbon in US agricultural soils. Soil Science Society of America Journal 66, 1249-1255.

Soong, J., Cotrufo, M.F., 2015. Annual burning of a tallgrass prairie inhibits C and N cycling in soil, increasing recalcitrant pyrogenic organic matter storage while reducing N availability. Global Change Biology 21, 2321-2333.

Stocker, T., Dahe, Q., Plattner, G.K., 2014. Climate Change 2013: The Physical Science Basis. WGI Fifth Assessment Report. Cambridge University Press.

Viscarra Rossel, R.A., Walvoort, D.J.J., McBratney, A.B., Janik, L.J., Skjemstad, J.O., 2006. Visible, near infrared, mid infrared or combined diffuse reflectance spectroscopy for simultaneous assessment of various soil properties. Geoderma 131, 59-75.

Weiland, J.J., Guyonnet, R., 2003. Study of chemical modifications and fungi degradation of thermally modified wood using DRIFT spectroscopy. . European Journal of Wood and Wood Products 61, 216-220.

Wiedemeier, D.B., Hilf, M.D., Smittenberg, R.H., Haberle, S.G., Schmidt, M.W.I., 2013. Improved assessment of pyrogenic carbon quantity and quality in environmental samples by high-performance liquid chromatography. Journal of Chromatography A 1304, 246-250.

Wiedemeier, D.B., Abiven, S., Hockaday, W.C., Keiluweit, M., Kleber, M., Masiello, C.A., McBeath, A.V., Nico, P.S., Pyle, L.A., Schneider, M.P.W., Smernik, R.J., Wiesenberg, G.L.B., Schmidt, M.W.I., 2015. Aromaticity and degree of aromatic condensation of char. Organic Geochemistry 78, 135-143.

Wood, D.J., 1988. Characterisation of Charcoals by DRIFT. Microchimica Acta 95, 167-169.

Wurster, C.M., Lloyd, J., Goodrick, I., Saiz, G., Bird, M.I., 2012. Quantifying the abundance and stable isotope composition of pyrogenic carbon using hydrogen pyrolysis. Rapid Communication in Mass Spectrometry 26, 2690-2696.

Wurster, C.M., Saiz, G., Schneider, M.P.W., Schmidt, M.W.I., Bird, M.I., 2013. Quantifying pyrogenic carbon from thermosequences of wood and grass using hydrogen pyrolysis. Organic Geochemistry 62, 28-32.

Ziolkowski, L.A., Chamberlin, A.R., Greaves, J., Druffel, E.R.M., 2011. Quantification of black carbon in marine systems using the benzene polycarboxylic acid method: a mechanistic and yield study. Limnology and Oceanography: Methods 9, 1541-5856.

Supplement Manuscript 3

Quantification of pyrogenic carbon in the environment: An integration of analytical approaches.

M. Francesca Cotrufo[1,2*], Claudia Boot[1,3], Samuel Abiven[4], Erika J. Foster[1,2], Michelle Haddix[1], Moritz Reisser[4], Christopher M. Wurster[5], Michael I. Bird[5] and Michael W. I. Schmidt[4]

1-Natural Resources Ecology Laboratory, Colorado State University, Fort Collins, Colorado

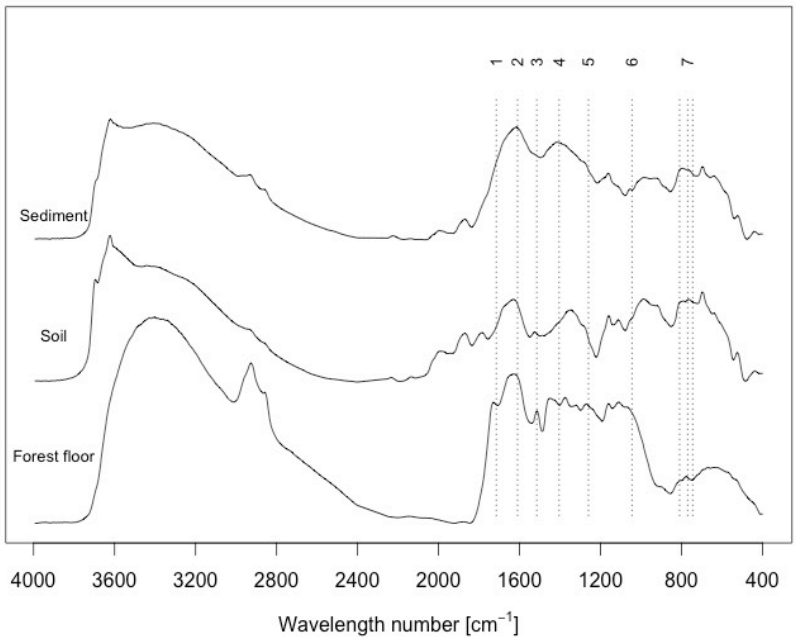
2-Department of Soil and Crop Sciences, Colorado State University, Fort Collins, Colorado

3-Department of Chemistry, Colorado State University, Fort Collins, Colorado

4-Soil Science and Biogeography Unit, University of Zurich, Zurich, Switzerland

5-College of Science, Technology and Engineering and Center for Tropical Environmental and Sustainability Science, James Cook University, Cairns, Queensland, Australia

*Corresponding Author: Francesca.cotrufo@colostate.edu



Supplementary Figure 1: Mid Infrared Spectra (MIR) of three different sample matrices. Numbers indicate major MIR adsorption bands (cm-1), , with description and in brackets the prevailing trend with increasing PyC: 1 = 1730-1680, Aromatic carbonyl/carboxyl C=O stretch (increase); 2 = 1610-1570, C=C stretch (increase); 3 = 1510-1500, Lignin, aromatic C=C stretch (decrease); 4= 1430-1380, Aromatic C=C stretch (increase); 5= 1260-1210, Cellulose (decrease); 6= 1060-1020, Aliphatic C-O- and alcohol C-O stretch (decrease); 7 =880, 805, 745, C-H aromatic bending deformation (increase).

Supplementary Table 1: List of Partial Least-Squares Regression (PLSR) factors for three different sample matrices, associated % variation accounted for, and predicted minimum residual sum of squares during validation (leave-one-out cross validation method)

Forest floor						
		1 comps	2 comps	3 comps	4 comps	5 comps
Hypy	% variance	81.4	88.4	91.6	95.6	97.0
	RMSE	7.1	6.8	6.6	6.7	6.7
BPCA	% variance	41.2	83.0	86.9	93.9	95.8
	RMSE	1.7	1.4	1.4	1.3	1.3
Soil						
		1 comps	2 comps	3 comps	4 comps	5 comps
Hypy	% variance	54.4	67.8	84.4	89.7	90.8
	RMSE	0.8	0.9	0.9	0.8	0.7

BPCA	% variance	43.7	75.3	82.3	88.6	91.1
	RMSE	0.4	0.2	0.2	0.2	0.1
Sediments						
		1 comps	2 comps	3 comps	4 comps	5 comps
Hypy	% variance	61.2	93.8	95.7	96.7	98.4
	RMSE	4.9	5.1	4.3	3.6	3.0
BPCA	% variance	64.0	82.0	92.2	93.8	96.5
	RMSE	4.3	3.5	3.4	3.4	3.4

Manuscript 4

The wayward decomposition behaviour of Pyrogenic Carbon in soils – pyrogenic carbon and grass degradation and related priming effect in tropical, temperate and arctic ecosystems

Moritz Reisser[1], Bernardo Maestrini[1,2], Maitane Iturrate-Garcia[3], Runi anak Sylvester Pungga[4], Samuel Abiven[1*]

1-Department of Geography, University of Zurich, Zurich, Zurich, Switzerland

2-Department of Forestry, Michigan State University, East Lansing, Michigan, USA

3-Department of Evolutionary Biology and Environmental Studies, University of Zurich, Zurich, Zurich, Switzerland

4-Forest Department of Sarawak, KM10, Jalan Datuk Amar Kalong Ningkan, 93250 Kuching, Sarawak, Malaysia

*Corresponding author: samuel.abiven@geo.uzh.ch

Contributions: S.A. and B.M. developed the experimental design. B.M. and M.R. conducted the field campaigns. M.I.G. and R.A.S.P. supported the fieldwork. M.R. collected and analysed the data. M.R., S.A., B.M. and M.I.G interpreted the data. M.R., S.A., B.M. and M.I.G contributed to the writing of the manuscript.

Submitted to: Scientific Reports, March 2018

Keywords: soil organic carbon, pyrogenic carbon, degradation pathways, arctic, temperate and tropical ecosystems.

Abstract

Pyrogenic carbon (PyC) is an important compound of the carbon (C) cycle because of its long resident times in soil and high potential to build up soil C stocks. The processes explaining its persistence remain largely unknown. Here we measured losses of a ^{13}C-enriched PyC and grass in ecosystems at different latitudes (arctic tundra, temperate forest and tropical rain forest) one to two years after its incorporation into the soil to investigate the influence of the ecosystem properties on C losses. Grass decomposition decreased along the ecosystem latitude, while we observed higher PyC losses in the temperate climate as compared to arctic and tropical ecosystems, which were comparable. These higher losses in the temperate forest correspond to a higher PyC recovery in heavy fractions, indicating that, despite a lower recovery, PyC may be more stabilised on the long term for this ecosystem. For all ecosystems, we observed a very important priming effect (-10 to +15% of the soil C affected) induced by PyC incorporation, but patterns could not be explained mechanistically. Our observations of persistence and priming effects of PyC are very surprising and not in line with previous findings. They challenge the current view on PyC degradation and call for new paradigms to model terrestrial carbon cycle.

Keywords: soil organic carbon, pyrogenic carbon, degradation pathways, artic, temperate and tropical ecosystems.

Introduction

Soils store more than three times as much carbon as the atmosphere[1] and represent an important aspect to be included in global earth system models[2,3]. Most models rely on ecosystem properties, like climate or soil characteristics, but particularly on temperature and precipitation patterns or more generalised latitudinal gradients[2,4–7]. Typically it is assumed that soil organic carbon (SOC) decomposition is positively correlated to temperature[8–13]. This behaviour is considered as very similar for all types of chemical compounds SOC is made of[9,14,15]. Out of all the molecules present in soil, organic carbon of pyrogenic origin (from wildfires or deliberate man-made pyrolysis; PyC) represents a major contribution of SOC content at a global level with in average more than 13 %[16,17]. Its persistence in soils for a much longer time than its precursor material make it unique by many aspects, but also difficult to integrate in large scale models[18–20]. The failure to account for the higher residence times of the PyC pool may result in an offset in current carbon feedbacks to climate change[3], and it is now urgent to incorporate it in land surface models. In addition to the decomposition of the material itself, both input of fresh litter material and PyC can lead to a priming effect (PE), i.e. an increased or decreased decomposition of the native SOC[21–23], which may influence the net carbon storage in soils, making carbon feedback predictions even more challenging.

To quantify PyC decomposition rate and induced PE across different ecosystems we conducted a field decomposition experiment in three different sites representing the largest global range of decomposition conditions: a tropical rainforest on Borneo, a temperate mixed forest in Switzerland and an arctic tundra in North-East Siberia (site overview in supplementary table 1). In each of these sites we added the same highly ^{13}C-labelled ryegrass (*Lolium perenne* L.*;* 4.88-6.90 atom % ^{13}C) and PyC produced from the same material to the soil. Thanks to the high ^{13}C enrichment of the input material and the large number of replicates we were able to robustly detect even small losses in the materials over the observed time period (one year in the tropical and temperate forests, two years in the artic ecosystem). We used grass, because this type of biomass is present in all the three ecosystems whereas woody materials are not present in significant amounts at the arctic site. For every site, grass and PyC added biomass were left to decompose in a semi closed system (see Figure 1 and according to ref. 24). Using a density fractionation method we could furthermore specify, whether the recovered input had been stabilized in the form of aggregates or

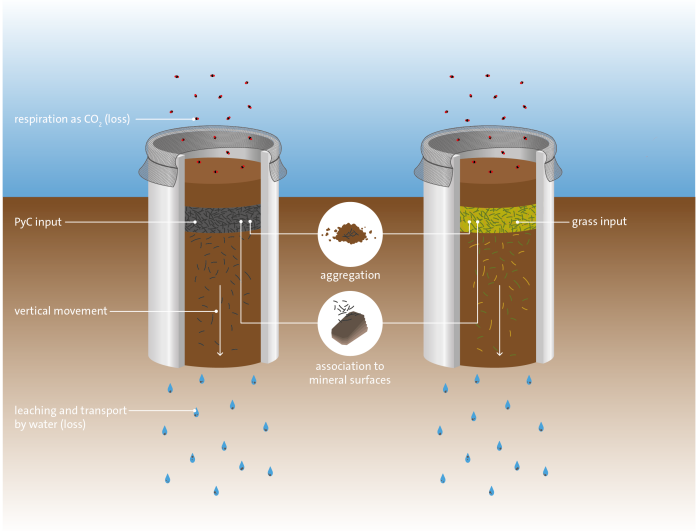


Figure 1: Conceptual framework of the experiments. Different pathways of the input materials are shown. Respiration, leaching and vertical transport beyond the depth of investigation cannot be disentangled and represent the overall losses. Vertical movement can be traced to a depth of 10 cm. Still untransformed and free material is found with density fractionation in the free light fraction (fLF); C in aggregates is derived from the occluded light fraction (oLF) and C which is bound on mineral surfaces is derived from the heavy fraction (HF). Density fractionation was applied in the first 3 cm of the soil, where the initial input had been placed and the majority of recovered material was expected. In the arctic no aggregation or mineral interaction could be found, because there was no mineral phase in the first 3 cm.

by mineral interactions[25]. We also divided the soil into different depth increments (0-3 cm, 3-6 cm and 6-10 cm) to estimate the downward translocation of our inputs. On every site, the material was left to decompose under two different conditions based on site-specific drivers of decomposition: drought in the tropics (normal conditions and rain reduction), pH in the temperate site (high and low pH) and soil moisture in the arctic (high water table, low water table). These different conditions were chosen to investigate if local parameters may be more important decomposition drivers than global ones.

Results

Site-specific drivers

We could successfully establish site-specific treatments in each dataset. At the tropical site, small rainout shelters led to a decrease in soil moisture of 18 ± 4 %, which would correspond to a decrease in rainfall of around 450 to 500 mm yr^{-1}. At the temperate site we measured a pH of 5.44 ± 0.45 for the low-pH half and 6.61± 0.36 for the other half. At the arctic site, the water table was continuously within the cylinders of the wetter half, while the drier half remained above the water table. We kept potentially other interfering drivers like climate or landform as identical as possible between treatments in each of the ecosystems. Despite the large differences between site-specific treatments however, we found no statistically significant difference in any of the parameters we measured (decomposition, priming effect, location of carbon in the physical fractions). Therefore we grouped the site-specific treatments together for further statistical analyses, reaching a number of 14 replicates for each treatment and so achieving a higher statistical power.

Total carbon input recovery

The losses of grass-C decreased with latitude, with lowest recoveries in the tropical site 12.6 ± 0.8 % (variation corresponds to the standard error) and lowest losses / highest recovery in the arctic (33.7 ± 0.8 % - fig. 2). We recovered 15.5 ± 1.8 % at the temperate site. The recovery in the arctic site was significantly different from the other two sites (p-value < 0.001). In contrast, PyC losses were not decreasing from tropics towards arctic. We found the highest PyC losses in the temperate site with a recovery of only 59.2 ± 1.7 %, which

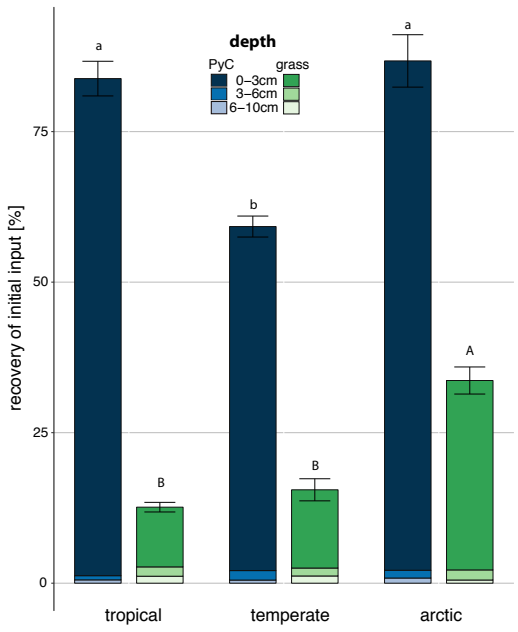


Figure 2: Recovery of initial input C per depth as % of the initial input C. Bars represent standard errors on the bulk recovery. Small letters indicate significant differences of PyC input between sites and capital letters indicate significant differences of grass input between sites (p-value < 0.001).

is significantly lower than for the other two sites (p-value < 0.001). We found no significant difference between the PyC recovered in the tropical (83.8 % ± 2.9 %) and the arctic site (86.7 ± 4.4 %). These results are very surprising and contradict largely the current literature on organic matter decomposition along climatic gradients[2,6,8,9].

Vertical transport

Vertical transport within the first 10 cm of soil was small for all ecosystems and inputs (figure 2). Recovery of grass in the second depth considered (3 – 6 cm) ranged from 1.3 ± 0.4 % in the temperate over 1.6 ± 0.1 % in the tropical to 1.7 ± 0.2 % in the arctic site. Smaller quantities were found below, in the depth of 6 - 10 cm: 0.5 ± 0.1 % in the arctic and 1.2 ± 0.3 % / ± 0.1 % for the temperate and tropical sites, respectively. The vertical distribution of the recovered PyC followed a similar pattern. Transport was even smaller with 0.7 ± 0.1 % recovery in the tropical, 1.3 ± 0.2 % in the arctic and 1.6 ± 0.5 % in the temperate site for the interval 3 – 6 cm and a recovery of 0.5 ± 0.2 % in the temperate, 0.6 ± 0.2 % in the tropical and 0.9 ± 0.5 % in the arctic site for the third depth increment.

We found no significant differences between the inputs and between the sites in the depths below 3 cm. Only minor proportions were transported vertically in the soil profile, unless they were transported below the maximum sampled depth (10 cm).

Associations with the soil

Our density fractionation method distinguished between untransformed material (fLF), organic material in aggregates (oLF) and material which is strongly bound on mineral surfaces (HF). A detailed description of the procedure is given in the material and methods section. Recovery of the input C in the density fractions is reported in figure 3. In the arctic site there was no mineral phase in the first depth increment, resulting in 100 % fLF for all samples. We found highest recovery rates for grass in the HF with 58 ± 5.1 % and 61 ± 6.6 % of the bulk recovery for the tropical and the temperate site, respectively. We found only 8.6 ± 3.4 % of the recovered material in the oLF of the tropical and 19 ± 6.8 % in the temperate soil. This difference can partly be explained by the much lower potential for aggregate formation in this very sandy tropical soil. The fLF, representing the rather unchanged input material was not more than 20 ± 5.3 % of the bulk recovery in the temperate and 33 ± 5.5 % in the tropical site or 3.3 ± 0.9 % and 3.7 ± 0.7 % of the total input, respectively.

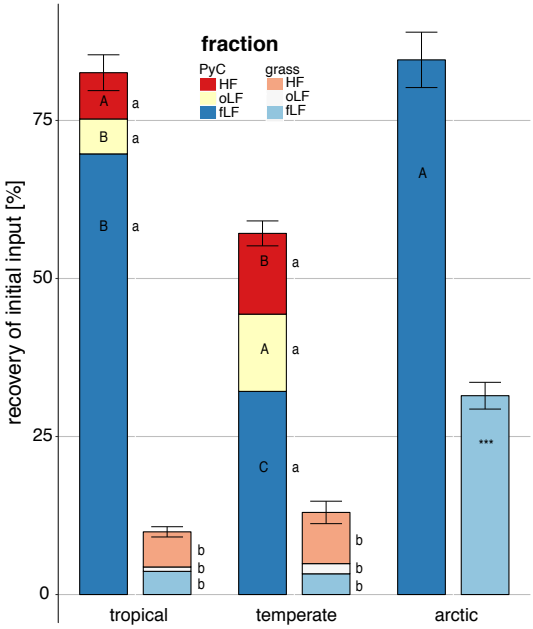


Figure 3: Recovery of initial input C as % of initial input C in the density fractions. fLF: free light fraction, oLF: occluded light fraction, HF: heavy fraction. Bars represent standard errors on the bulk fractions, i.e. the recovery of the first depth increment (0-3 cm). Small letters indicate significant differences between PyC and grass input within each site (p-value < 0.001), capital letters indicate significant differences of the PyC input between the sites (p-value < 0.05) and the asterisks indicate a significant difference between the grass recovery of Siberia and the other two sites (p-value < 0.001).

For the PyC input, the picture looks very different. The majority of PyC is still in the fLF form, i.e. 84 ± 2.6 % of the bulk recovery in the tropical and 56± 3.7 % in the temperate soil. The HF form contained only 9.2 ± 1.5 % of recovered PyC in the tropical site and 23 ± 3.0 % in the temperate site. The oLF contained 6.8 ± 2.6 % of recovered PyC in the tropical forest and 22 ± 3.0 % in the temperate forest. Thus 32 % of the initial input PyC was still untransformed after one year at the temperate site as compared to 4 % for grass.

Priming effect

We found large bulk PEs for both input materials and both sites as shown in figure 4a (since there was virtually only organic material and we calculated the PE on the change of the total carbon concentration in the samples, in contrast to more commonly used respiration measurements, the evaluation for the arctic site was not possible). In the tropical soil we find in average no PE with PyC, but a positive priming of 9.7 ± 11.6 % native SOC decrease with the grass input. On the temperate site on the other hand, we observe a negative PE for both inputs with 14.1 ± 9.5 % and 9.8 ± 5.0 % increase of native SOC for PyC and grass, respectively. This is opposite to previous findings with wood derived PyC on the same site[26]. The variability is very important, as presented by the standard errors of the bulk values. They are especially large in the tropical soil for both inputs despite the high numbers of replicates. Since our design captured the spatial heterogeneity by placing the

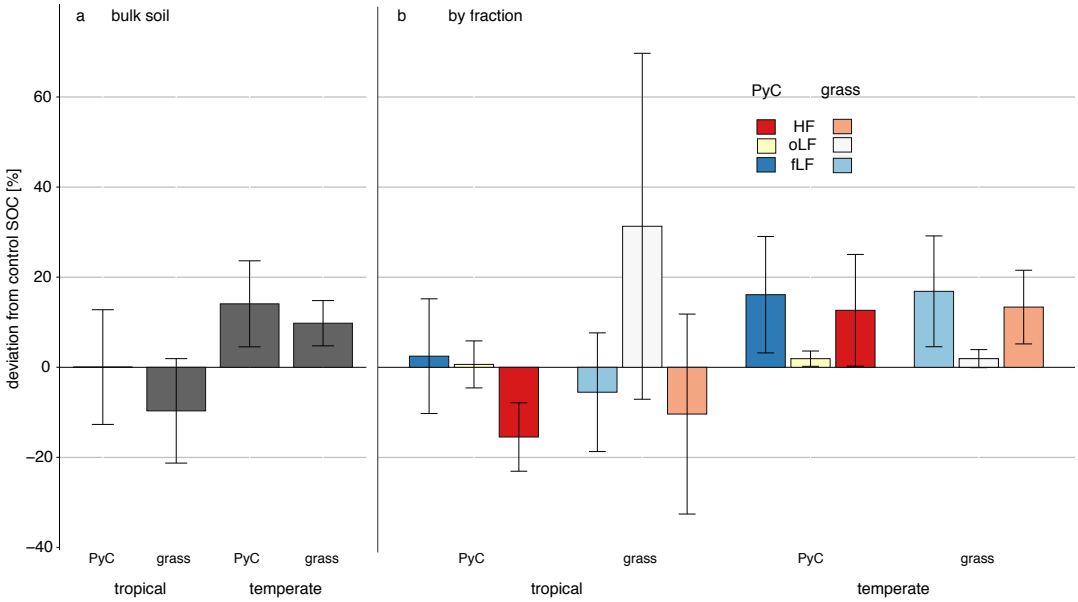


Figure 4: Priming effect in the tropical and temperate site shown as the relative change (%) of the SOC at the end of the experiment compared to the control treatment. These results are not representing mineralization rates, but only how SOC stocks developed over time after the initial input. Bars show a) the bulk samples and b) the density fractions; fLF: free light fraction, oLF: occluded light fraction, HF: heavy fraction. Whiskers represent the standard error.

control samples close to the respective input samples, variations can hardly be attributed to a general spatial heterogeneity but in fact rather mirror a great variability in the PE itself. This large variability is even more prominent in the results for the different density fractions (figure 4b). On the tropical site, PyC input seems to inhibit decomposition in the fLF with 2.5 ± 12.7 % increased native SOC content but triggered on the other side the decomposition of organic matter, that was bound on minerals with a decrease of 15.5 ± 7.6 % in the HF. Grass input however seems to promote the formation of aggregates while generally increasing decomposition, leading to positive priming in fLF (5.5 ± 13.2 %) and HF (10.4± 22.2 %). In the temperate soil, both inputs produced negative priming in all fractions with highest changes in native SOC in the fLF (16.1 ± 12.9 % and 16.8 ± 12.3 % for PyC and grass, respectively) and smallest changes in the oLF (1.9 ± 1.7 % and ± 2.0 % for PyC and grass), meaning that decomposition was generally slowed down.

Discussion

Site-specific drivers

The lack of significant differences between the site-specific treatments (moisture and pH) is surprising for two main reasons. Firstly, our introduced treatments varied much more than other potential drivers or co-variants, since the variability of the latter was minimized through our design. Secondly, an important body of literature highlights that PyC could be affected by both pH and moisture. The pH value was shown to significantly influence PyC content at the global scale[16]. At the process scale, PyC has been shown to fragment faster under alkaline conditions, which could lead to a better incorporation into the soil and subsequent stabilization[27]. Laboratory studies showed an influence of pH on the degradation of organic carbon in general[28,29]. The absence of this effect in our soils might indicate that the main difference is between acidic and alkaline soils, while our soils were in the acidic and neutral ranges . Soil moisture seems to be equally important for the degradation pathways of PyC[30]. A study along a climosequence found significantly higher PyC contents in wetter soils, than in dry soils[31]. Furthermore, the influence of moisture on the degradation of organic carbon in general was already described extensively[8,32,33]. Our results seem to contradict previous studies, in particular those studying global scales. One major difference is that we could keep potential co-variates relatively constant in our experiments, while this is not the case for global studies. Global observations inherently can not differentiate between all possible drivers, e.g. pH might just be a proxy for a more complex set of ecosystem properties[34], and it is rather these ecosystem properties which in turn drive C. Thus, a valuable explanation for the results of global studies and this one, could be that pH and soil moisture are much less important for SOC and specifically PyC dynamics, but rather some (to be identified) co-variate.

Degradation of input

Generally, the recovery rates we observe here are very low (i.e. the losses were high), when compared to other PyC decomposition studies[18,24,35], even if compared to results with high losses[36]. One reason could be that we studied grass derived pyrogenic matter, whereas in most other studies the precursor material was wood. In fact, grass-derived PyC is chemically and physically less stable, as it does not

contain lignified structures. These lignified structures usually lead to a higher C/O and C/H ratio, as well as a higher aromaticity[37–39] in the PyC which makes it chemically[40] and physically[41] more resistant to degradation. The few studies with grass-derived PyC are laboratory incubations, which might not be directly comparable to a field setup[35,42].

Concerning the recovery across the vertical profile of the samples, our dataset lies within the range of other values calculated for vertical transport. Other studies observed that between 0.45 and 8 % of the input material migrated below the incorporation depth[26,43,44] in the same timeframe.

In a recent review, ref [45] proposed the following processes to explain the PyC losses in a soil: erosion, transport, biotic and abiotic oxidation, solubilisation and fragmentation. Losses described here have to be explained by a different combination of these processes in each ecosystem. In the arctic site, organic matter input does not come in contact with soil minerals, i.e. any possible stabilization within the matrix. Most of the other mechanisms are rather limited in this system. Erosion and transport by wind are ruled out by our experimental setup (but may take place otherwise). Vertical transport by water is unlikely, since the water is stagnant in this system, so transport would be largely limited to diffusion. Break down through freeze thawing can definitely play a role, but can only occur during very short spring and fall seasons. Furthermore, the high water saturation levels favour anaerobic conditions. Lastly, the extremely low temperatures make decomposition rate equivalent to null during three quarters of the year. The differences between grass and PyC are most probably mainly driven by the inherent chemical properties and the potential to be solubilized.

On the tropical site, where climatic conditions are opposite to those in the arctic, grass is lost much faster. This corresponds to a combination of high microbial activity and higher water movement through the soil. Although the low recoveries in lower depths do not support the hypothesis of vertical movement in the form of particles, it is still possible that part of the C was translocated in the form of dissolved organic carbon, and thus had already left our system before sampling. This fraction is probably small for PyC at the incorporation in the soil, but may increase with PyC ageing[46]. Under these conditions, PyC fragmentation, which has been found in many publications on biochar (ref [47] and references therein), cannot be related to freeze-thawing cycles or cryoturbation. Another hypothesis is related to microbial biomass:

the microbial community existing in the tropical forest may not be adapted to fire-derived material, since fire disappeared from this particular ecosystem several millennia ago[48]. PyC as input might even behave toxic to some microbes[49]. However, this effect would not last long enough to create the large differences we observed.

Compared to the two other sites, the temperate forest presents a very different pattern: even though the labile grass material follows the latitudinal gradients trend with highest losses in the tropics and lowest in the arctic we find high losses of PyC input. In this ecosystem, all the possible loss mechanisms listed above may have occurred. In fact, this site is characterized by relatively high amounts of rainfall for leaching (although we only observed a limited vertical transport), a long winter season with temperatures around the melting point that can promote freeze-thawing fractionation processes, and high organic matter inputs through yearly litter fall to sustain soil microbial activity. It is also possible that microbes can better adapt to PyC input, compared to the arctic and tropical site where fires do not occur so often. The combination of all these processes might be the reason for the high losses, rather than only one of them.

Stabilization pathways

Even though we find evidence of very fast degradation of PyC after one year at the temperate site, this does not necessarily mean low stabilization at the same time. In fact, we find here that in this place of lowest recoveries we also find highest incorporation into aggregates and on mineral surfaces, indicating strong stabilization pathways. We can distinguish between three different stabilizing mechanisms: inherent chemical recalcitrance, physical disconnection and physic-chemical interactions[25]. Chemical recalcitrance is defined by the inherent chemical properties of PyC, which make it resistant to oxidation and other chemical processes, mainly through a high aromaticity and high C/H and C/O ratios[40,50,51]. This recalcitrance is the only form inhibiting degradation at the untransformed stage but continues to play a role in combination with the other two mechanisms. However, since chemical properties of the input material were kept constant in all sites, recalcitrance cannot lead to differences in our results.

Physical disconnection is the separation of decomposers or oxygen from the input material mainly via aggregation[26,52] and is indicated by the oLF from the density fractionation. Physico-chemical interactions with minerals are the strongest

stabilization pathways in particular for PyC through its abundant negatively charged functional groups[53] and electrochemical properties[54]. Therefore, clay minerals, with its abundant positively charged surfaces are strongly supporting these interactions[55–58]. Both of these two pathways are already strongly developed in the temperate soil, leading to presumably very efficient long-term persistence of PyC in the soil[56,59]. While processes like fragmentation might lead to an initial fast degradation of PyC[27,60], it might at the same time foster the possibilities of stabilization through better incorporation into the mineral matrix and higher specific surface areas. Therefore, in order to capture the dynamics of PyC in any ecosystem it is important to account for all degradation and stabilization pathways. Processes like vertical translocation, physical protection or fragmentation, leaching, chemical transformation, binding to minerals as well as microbial decomposition may take place with a different intensity in different ecosystems. As these processes are driven by other variables than only climate, being more complex than often assumed in global models, it is crucial to consider other ecosystem properties like soil properties for modelling of PyC persistence, as well.

Priming Effect

Stabilization was not only apparent for the input material, but even affected the native organic carbon as seen in the negative PE for the bulk and fractionated samples. Thus, at the temperate site we see a “two-way” stabilization of both input and native material, summing up to a very important and significant effect. Since our measured priming does not constitute a value of instantaneous mineralization, but rather represents the cumulative change in stocks priming is here expressed in the same unit as stocks and is therefore directly comparable to it), we can directly attribute both input and native carbon to an increase in C stock. PE was even in the same range of stock change than the input itself with 10-15 % increase of stock each, representing the equivalent of 30 years fixed by the 4p1000 initiative (www.4p1000.org). These high values, higher than reported in the literature[22] up to now, can be explained by the methods we used: the stock related approach of measuring the PE and the use of highly ^{13}C labelled material, which enabled us to measure changes very precisely.

However, our results show that natural variability of PE is very high, when observed in the field with high ^{13}C signal to be measured in the bulk material. Most studies on PE, which are mainly carried out in the lab[22,35,49] with homogenized soils. A highly controlled environment can likely not capture the actual spread of results as we

observe it in the field. Since our design minimized spatial heterogeneity for larger than 15 cm distance, the remaining variability has to be attributed to very small-scale differences. Such differences are likely induced by microbial activity, which can vary at much smaller scales than what we are looking at.

Our study shows that PE is quantitatively large but the directions and seem to be very difficult to predict through such kind of field trials. This poses the challenge to constrain the PE for global C models.

Conclusions

The decomposition of PyC does not follow the regular patterns of organic matter decomposition as seen with plant material. It seems like a combination of processes, biotic and abiotic, explains better the changes in PyC content in soil than only the temperature and moisture used in many models and that this combination is probably different than for other organic C forms. This finding challenges our mechanistic understanding of SOC decomposition and its stabilization, but also the implementation of such an important organic compartment into global carbon cycle models. We also observed high values of priming effect, without being able to predict the amplitude and the direction of this priming effect in a given context. Considering the extent of this priming effect in term of C stock variations, one needs to consider ways to integrate this mechanism into large models. New approaches, like the use of highly labelled material, can be used to estimate this priming effect, but new hypothesis are needed in order to predict it.

Methods

Sites

The field site on the island of Borneo is located in the pristine tropical rainforest of Lambir National Park (4°12' N, 114°02' E), around 30 km south of Miri, Sarawak, Malaysia. Mean annual air temperature (MAAT) lies around 27 °C and mean annual precipitation (MAP) around 2740 mm[61]. The geology is dominated by sand- and shales and soils are mostly Acrisols or Arenosols (all soil classifications according to World Reference Base; WRB)[62]. The site we chose lies on an Arenosol and on a slope of approximately 3-10 °.

The Swiss Site is located on the south slope Lägeren Mountain with mixed temperate forest cover, on 20 km northwest of Zurich, Switzerland (47°29' N, 8°22' E). MAAT is 8.4 °C and MAP is 930 mm[63]. The site is divided into two geologies. The northern part lies on limestone and is classified as a Leptosol. The lower site lies on Tertiary sediments and shows more developed Cambisols[64]. Slope is around 10 °.

The Siberian site is located close to the arctic sea in the Kytalyk nature reserve, Yakutia, Russia (70°49' N, 147°28' E). The MAAT lies at -13.1 °C and the MAP is 232 mm[65]. There is continuous permafrost and the growing season is very short (mid-June to end-August)[65]. Vegetation cover is comprised of tundra sedges, mosses and dwarf shrubs. The mineral soil was usually covered with a thick layer of moss and often was below the water table. The site is flat, except for the topography characteristic of polygonal tundra[66] where drier polygonal ridges (1-1.5 m higher) alternate with depressed polygons that are water logged for most of the year. The soil type is a Histic Cryosol. A summary of the site characteristics is also given in supplementary table 2.

We do emphasize here that the selected sites are neither meant to represent robustly the respective ecosystems nor serve to upscale our results. They rather represent extreme conditions or "end-members" of global ecosystems to provide a large range of ecosystem properties.

Design

We placed a total of 42 steel cylinders (7 cm diameter, 12 cm height) into the soil of each field-site (giving 7 field replicates per material and treatment), such that roughly 2 cm would still be on the surface. The input material was then buried in the first 3 cm of the soil. Cylinders are open on top and bottom. We removed all aboveground material in the cylinders and covered them with a fine mesh to prevent litter input or erosion by wind or lateral transport, but being permeable by water. One third of the cylinders served as control, one third received grass input and one third received grass-PyC. In the temperate and tropical sites, the samples were always put in groups of three, such that one control, one grass and one PyC sample were close together (≤ 15 cm from each other) to minimize the effect of spatial heterogeneity.

Every site was further divided into two site-specific treatments, which accounted for critical drivers of decomposition in the respective place. In the tropical site we installed little rainout shelters, to simulate drought. In the temperate site we used the

apparent geological division to carry out a pH treatment. pH was measured in H_2O with a soil to water ratio of 1:2.5. At the arctic site the water table served as natural treatment. We chose small ridges and depressions in the landscape for the treatment. Input material corresponding to 0.345 g of C were put 1 cm below the soil surface (except the arctic, where it stayed on top) and left to decompose for exactly 1 year. At the arctic site it stayed 2 years, since the growing season is comparably very short and we feared that losses might be too small to detect after only one year.

For the sampling, the filling of the cylinders was divided into 0-3 cm, 3-6 cm and 6-10 cm. Every sample was air-dried and sieved to 2 mm (except arctic), where a part was taken for the density fractionation, and milled for subsequent analyses.

Moisture and temperature Data

Soil moisture and temperature in the soil (6 cm depth) were monitored using TMS-3 sensors (Tomst, Praha, Czech Republic) with a measurement interval of 15 min over the whole period. Two sensors were placed on the Lägeren site in- and outside of a cylinder to check for differences. Temperature below soil surface inside the cylinder was in average 0.08 °C (sd= 0.68 °C) warmer than without cylinder, which lies within the measurement uncertainty of the sensors. Soil moisture content was in average 14 % (sd = 8 %) lower inside of the cylinder, indicating, that there was slightly less water going into the cylinder than under natural conditions. Therefore, we can argue that overall conditions in the cylinders were very close to undisturbed natural soil, facilitating interpretation and enhancing robustness of the results. In Borneo two sensors were placed to check the effect of the rainout shelters.

Labelling and Measurement of the materials

The perennial ryegrass was grown in the MICE chamber[67] at the University of Zurich with CO_2 having 10 % ^{13}C and had been exposed to enriched CO_2 since sprouting to ensure homogenous labelling. These resulted in ^{13}C enrichment of the grown grass between 4.88 and 6.9 atom %. Part of the grass was then pyrolysed under continuous N_2 flow at 450 °C for 4h. Carbon content and the ^{13}C signal were measured with a Picarro device (Picarro Inc. California, USA) on-line with a combustion module with a running temperature of 950 °C.

Recovery of the input carbon was calculated with a two-pool mixing model (1) of the form:

$$m_{recover} = \frac{f_{sample} * m_{sample} - f_{control} * m_{sample}}{f_{material} - f_{control}} \quad (1)$$

where $m_{recover}$ is the mass of labelled input C that is still there, f_{sample} is the ^{13}C atom fraction in the taken sample, m_{sample} is the mass of the sample, $f_{control}$ is the ^{13}C atom fraction of the closest control sample, and $f_{material}$ is the ^{13}C atom fraction of the input material.

Density Fractionation

We used the density fractionation procedure of a similar study, which was already performed on the Swiss field site[26]. The method was done on all 0-3 cm subsamples of the Borneo and Swiss site. Briefly, 10 g of sample were mixed with 50 ml of a 1.6 g cm^{-3} sodium polytungstate (SPT) density solution, shaken and allowed to settle for 30 min. They were then centrifuged and the floating material ($\rho \leq 1.6$ g cm^{-3}) was filtered, washed, freeze-dried and milled for Picarro analysis as the free light fraction (fLF). The residue was then mixed again with 50 ml SPT solution, mixed and submitted to ultrasonic dispersion to yield the occluded light fraction (oLF). We used a sonifier (Bandelin Sonoplus HD 3400, Berlin, Germany) and a disruptive energy of 250 J ml^{-1} per sample. After sonification, the procedure was the same as for the fLF before. The remaining pellet of each sample was then washed thoroughly with H_2O, air dried and milled, to yield the heavy fraction (HF).

Priming

The priming was calculated by comparing the native carbon of the samples that had received input to the closest control sample (i.e. generally ≤ 15 cm apart), calculating the relative difference as shown in equation (2), where $C_{control}$ is the carbon content of the closest control sample, $C_{treatment}$ is the carbon content of the sample, corrected for the respective carbon input.

$$PE\ [\%] = \frac{C_{treatment} - C_{control}}{C_{control}} * 100 \quad (2)$$

Native carbon was normalized for the bulk samples on a concentration of g kg^{-1} for comparability using a weighed average over the different depth subsamples, as the bulk dry density was not consistent. This method differs from the generally applied methods of measuring the CO_2 outflux of the soil in the way, that it integrates the complete effect of priming over the whole period, instead of discrete points in time.

Statistics

We used R statistical software (R 3.4.1; ref [68]) to perform multiple-way analyses of variance (ANOVA) on the ^{13}C recovery and on the priming. Residues of the model were checked for normal distribution. Subsequent tukey-corrected pairwise least square means comparison was used as post-hoc test to check the hierarchy within the predictors on a level of significance = 0.05, using the package lsmeans for R.

Acknowledgement

We thank Eri Yamasaki, Gabriela Schaepman-Strub, Sergey Asanajev and Jonas Rudin for the help at the sites and the fieldwork. We greatly acknowledge the Department of Forestry, Sarawak, Malaysia, the Institute for Biological Problems of the Cryolithozone, Siberian Branch of Russian Academy of Science, Yakutsk, Russian Federation and the Swiss Federal Institute for Forest, Snow and Landscape Research for the possibility to conduct the fieldwork as well as for the logistical support. We thank Mirjam Studer for the help with the MICE facility to grow and label our grass. This research is supported by the University of Zurich through the University Research Priority Program on Global Change and Biodiversity.

Additional Information

Author Contributions

S.A. and B.M. developed the experimental design. B.M. and M.R. conducted the field campaigns. M.I.G. and R.A.S.P. supported the field work. M.R. collected and analysed the data. M.R., S.A., B.M. and M.I.G interpreted the data. M.R., S.A., B.M. and M.I.G contributed to the writing of the manuscript.

Competing Interests

The authors declare no competing interests.

.

References

1. IPCC. *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*. (2013).
2. Davidson, E. A. & Janssens, I. A. Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. *Nature* **440,** 165–173 (2006).
3. Lehmann, J. *et al.* Australian climate-carbon cycle feedback reduced by soil black carbon. *Nat. Geosci.* **1,** 832–835 (2008).
4. Heimann, M. & Reichstein, M. Terrestrial ecosystem carbon dynamics and climate feedbacks. *Nature* **451,** 289–292 (2008).
5. Cox, P. M., Betts, R. a, Jones, C. D., Spall, S. a & Totterdell, I. J. Acceleration of global warming due to carbon-cycle feedbacks in a coupled climate model. *Nature* **408,** 184–187 (2000).
6. Knorr, W., Prentice, I., House, J. & Holland, E. Long-term sensitivity of soil carbon turnover to warming. *Nature* **433,** 298–301 (2005).
7. Chen, S., Huang, Y., Zou, J. & Shi, Y. Mean residence time of global topsoil organic carbon depends on temperature, precipitation and soil nitrogen. *Glob. Planet. Change* **100,** 99–108 (2013).
8. Carvalhais, N. *et al.* Global covariation of carbon turnover times with climate in terrestrial ecosystems. *Nature* **514,** 213–217 (2014).
9. Fang, C., Smith, P., Moncrieff, J. B. & Smith, J. U. Similar response of labile and resistant soil organic matter pools to changes in temperature. *Nature* **433,** 57–9 (2005).
10. Schlesinger, W. & Andrews, J. Soil respiration and the global carbon cycle. *Biogeochemistry* **48,** 7–20 (2000).
11. Reichstein, M. *et al.* Modeling temporal and large-scale spatial variability of soil respiration from soil water availability, temperature and vegetation productivity indices. *Global Biogeochem. Cycles* **17,** 11–15 (2003).
12. Raich, J. W. & Potter, S. Global patterns of carbon dioxide emissions from

soils. *Global Biogeochem. Cycles* **9,** 23–36 (1995).

13. Crowther, T. *et al.* Quantifying global soil C losses in response to warming. *Nature* **104,** 104–108 (2016).

14. Fierer, N., Craine, J. M., McLauchlan, K. & Schimel, J. P. Litter Quality and the Temperature Sensitivity of Decomposition. *Ecology* **86,** 320–326 (2005).

15. Kirschbaum, M. U. F. The temperature dependence of soil organic matter decomposition, and the effect of global warming on soil organic C storage. *Soil Biol. Biochem.* **27,** 753–760 (1995).

16. Reisser, M., Purves, R. S., Schmidt, M. W. I. & Abiven, S. Pyrogenic Carbon in Soils: A Literature-Based Inventory and a Global Estimation of Its Content in Soil Organic Carbon and Stocks. *Front. Earth Sci.* **4,** 1–14 (2016).

17. Schmidt, M. W. I., Noack, A. G. & Osmond, G. Black carbon in soils and sediments: Analysis , distribution , implications , and current challenges. *Global Biogeochem. Cycles* **14,** 777–793 (2000).

18. Singh, N., Abiven, S., Torn, M. S. & Schmidt, M. W. I. Fire-derived organic carbon in soil turns over on a centennial scale. *Biogeosciences* **9,** 2847–2857 (2012).

19. Baldock, J. A. & Smernik, R. J. Chemical composition and bioavailability of thermally altered Pinus resinosa (Red pine) wood. *Org. Geochem.* **33,** 1093–1109 (2002).

20. Hammes, K., Torn, M. S., Lapenas, a. G. & Schmidt, M. W. I. Centennial black carbon turnover observed in a Russian steppe soil. *Biogeosciences Discuss.* **5,** 661–683 (2008).

21. Bingeman, C. W., Varner, J. E. & Martin, W. P. The Effect of the Addition of Organic Materials on the Decomposition of an Organic Soil. *Soil Sci. Soc. Am. J.* **17,** 34–38 (1953).

22. Maestrini, B., Nannipieri, P. & Abiven, S. A meta-analysis on pyrogenic organic matter induced priming effect. *GCB Bioenergy* **7,** 577–590 (2014).

23. Wang, J., Xiong, Z. & Kuzyakov, Y. Biochar stability in soil: Meta-analysis of decomposition and priming effects. *GCB Bioenergy* **8,** 512–523 (2016).

24. Maestrini, B. *et al.* Carbon losses from pyrolysed and original wood in a forest

soil under natural and increased N deposition. *Biogeosciences* **11,** 5199–5213 (2014).

25. von Lützow, M. *et al.* SOM fractionation methods: Relevance to functional pools and to stabilization mechanisms. *Soil Biol. Biochem.* **39,** 2183–2207 (2007).

26. Singh, N. *et al.* Transformation and stabilization of pyrogenic organic matter in a temperate forest field experiment. *Glob. Chang. Biol.* **20,** 1629–1642 (2014).

27. Braadbaart, F., Poole, I. & van Brussel, A. A. Preservation potential of charcoal in alkaline environments: an experimental approach and implications for the archaeological record. *J. Archaeol. Sci.* **36,** 1672–1679 (2009).

28. Aciego Pietri, J. C. & Brookes, P. C. Relationships between soil pH and microbial properties in a UK arable soil. *Soil Biol. Biochem.* **40,** 1856–1861 (2008).

29. Kemmitt, S. J., Wright, D., Goulding, K. W. T. & Jones, D. L. pH regulation of carbon and nitrogen dynamics in two agricultural soils. *Soil Biol. Biochem.* **38,** 898–911 (2006).

30. Ascough, P., Bird, M., Meredith, W., … C. S.-F. in E. & 2018, undefined. Dynamics of Charcoal Alteration in a Tropical Biome: A Biochar-Based Study. *Frontiersin.Org* **6,** (2018).

31. Glaser, B. & Amelung, W. Pyrogenic carbon in native grassland soils along a climosequence in North America. *Global Biogeochem. Cycles* **17,** (2003).

32. Doetterl, S. *et al.* Soil carbon storage controlled by interactions between geochemistry and climate. *Nat. Geosci.* **8,** 780–783 (2015).

33. Moyano, F. E. *et al.* The moisture response of soil heterotrophic respiration: Interaction with soil properties. *Biogeosciences* **9,** 1173–1182 (2012).

34. Schmidt, M. W. I. *et al.* Persistence of soil organic matter as an ecosystem property. *Nature* **478,** 49–56 (2011).

35. Kuzyakov, Y., Subbotina, I., Chen, H., Bogomolova, I. & Xu, X. Black carbon decomposition and incorporation into soil microbial biomass estimated by 14C labeling. *Soil Biol. Biochem.* **41,** 210–219 (2009).

36. Zimmermann, M. *et al.* Rapid degradation of pyrogenic carbon. *Glob. Chang.*

Biol. **18,** 3306–3316 (2012).

37. Budai, A. *et al.* Effects of pyrolysis conditions on Miscanthus and corncob chars: Characterization by IR, solid state NMR and BPCA analysis. *J. Anal. Appl. Pyrolysis* **128,** 335–345 (2017).

38. Chatterjee, S. *et al.* Elucidating the chemical structure of pyrogenic organic matter by combining magnetic resonance, mid-infrared spectroscopy and mass spectrometry. *Org. Geochem.* **51,** 35–44 (2012).

39. Czimczik, C. I., Preston, C. M., Schmidt, M. W. I., Werner, R. A. & Schulze, E. D. Effects of charring on mass, organic carbon, and stable carbon isotope composition of wood. *Org. Geochem.* **33,** 1207–1223 (2002).

40. McBeath, A. V., Smernik, R. J., Krull, E. S. & Lehmann, J. The influence of feedstock and production temperature on biochar carbon chemistry: A solid-state 13C NMR study. *Biomass and Bioenergy* **60,** 121–129 (2014).

41. Pignatello, J. J., Uchimiya, M., Abiven, S. & Schmidt, Michael, W. I. in *Biochar for Environmental Management - Science, Technology and Implementation* (eds. Lehmann, J. & Joseph, S.) 195–233 (Routledge, 2015).

42. Maestrini, B., Herrmann, A. M., Nannipieri, P., Schmidt, M. W. I. & Abiven, S. Ryegrass-derived pyrogenic organic matter changes organic carbon and nitrogen mineralization in a temperate forest soil. *Soil Biol. Biochem.* **69,** 291–301 (2014).

43. Major, J., Lehmann, J., Rondon, M. & Goodale, C. Fate of soil-applied black carbon: Downward migration, leaching and soil respiration. *Glob. Chang. Biol.* **16,** 1366–1379 (2010).

44. Hilscher, A. & Knicker, H. Degradation of grass-derived pyrogenic organic material, transport of the residues within a soil column and distribution in soil organic matter fractions during a 28month microcosm experiment. *Org. Geochem.* **42,** 42–54 (2011).

45. Bird, M. I., Wynn, J. G., Saiz, G., Wurster, C. M. & McBeath, A. The Pyrogenic Carbon Cycle. *Annu. Rev. Earth Planet. Sci.* **43,** 273–98 (2015).

46. Abiven, S., Hengartner, P., Schneider, M. P. W., Singh, N. & Schmidt, M. W. I. Pyrogenic carbon soluble fraction is larger and more aromatic in aged charcoal than in fresh charcoal. *Soil Biol. Biochem.* **43,** 1615–1617 (2011).

47. Lehmann, J. *et al.* Biochar effects on soil biota - A review. *Soil Biol. Biochem.* **43,** 1812–1836 (2011).

48. Bowman, D. M. J. S. *et al.* Fire in the Earth System. *Science (80-.).* **324,** 481–484 (2009).

49. Ahn, M.-Y., Zimmerman, A. R., Gao, B. & Ahn, M.-Y. Positive and negative carbon mineralization priming effects among a variety of biochar-amended soils. *Soil Biol. Biochem.* **43,** 1169–1179 (2011).

50. Lehmann, J. *et al.* in *Biochar for Environmental Management - Science, Technology and Implementation* (eds. Lehmann, J. & Joseph, S.) 235–282 (Routledge, 2015).

51. Wiedemeier, D. B. *et al.* Aromaticity and degree of aromatic condensation of char. *Org. Geochem.* **78,** 135–143 (2015).

52. Ekschmitt, K. *et al.* Soil-carbon preservation through habitat constraints and biological limitations on decomposer activity. *J. Plant Nutr. Soil Sci.* **171,** 27–35 (2008).

53. Mao, J.-D. *et al.* Abundant and Stable Char Residues in Soils Implications for Soil Fertility and Carbon Sequestration.pdf. (2012). doi:10.1021/es301107c

54. Joseph, S. *et al.* Shifting paradigms: development of high-efficiency biochar fertilizers based on nano-structures and soluble components. *Carbon Manag.* **4,** 323–343 (2013).

55. Hassink, J. The capacity of soils to preserve organic C and N by their association with clay and silt particles. *Plant Soil* **191,** 77–87 (1997).

56. Six, J., Conant, R. T., Paul, E. A. & Paustian, K. Stabilization mechanisms of soil organic matter: Implications for C-saturation of soils. *Plant Soil* **241,** 155–176 (2002).

57. Merckx, R., den Hartog, A. & van Veen, J. A. Turnover of root-derived material and related microbial biomass formation in soils of different texture. *Soil Biol. Biochem.* **17,** 565–569 (1985).

58. Sørensen, L. H. Stabilization of newly formed amino acid metabolites in soil by clay minerals. *Soil Sci.* **114,** (1972).

59. Torn, M. S., Trumbore, S. E., Chadwick, O. A., Vitousek, P. M. & Hendricks, D.

M. Mineral control of soil organic carbon storage and turnover. *Nature* **389,** 170–173 (1997).

60. Spokas, K. A. *et al.* Physical Disintegration of Biochar: An Overlooked Process. *Environ. Sci. Technol. Lett.* **1,** 326–332 (2014).

61. Kumagai, T. *et al.* Annual water balance and seasonality of evapotranspiration in a Bornean tropical rainforest. *Agric. For. Meteorol.* **128,** 81–92 (2005).

62. An, S. T. *et al.* — Mini Review — Review of Soils on the 52 ha Long Term Ecological Research Plot in Mixed Dipterocarp Forest at Lambir , Sarawak , Malaysian Borneo. *Tropics* **18,** 61–86 (2009).

63. Ruehr, N. K. & Buchmann, N. Soil respiration fluxes in a temperate mixed forest: Seasonality and temperature sensitivities differ among microbial and root-rhizosphere respiration. *Tree Physiol.* **30,** 165–176 (2009).

64. Heim, A., Wehrli, L., Eugster, W. & Schmidt, M. W. I. Effects of sampling design on the probability to detect soil carbon stock changes at the Swiss CarboEurope site Lägeren. *Geoderma* **149,** 347–354 (2009).

65. Iturrate-Garcia, M. *et al.* Interactive effects between plant functional types and soil factors on tundra species diversity and community composition. *Ecol. Evol.* **6,** 8126–8137 (2016).

66. Schirrmeister, L., Pestryakova, L., Wetterich, S. & Tumskoy, V. Joint Russian-German polygon project : East Siberia 2011 - 2014 ; the expedition Kytalyk 2011. *Berichte zur Polar- und Meeresforschung = Reports on polar and marine research* **653,** (2012).

67. Studer, M. S. *et al.* The MICE facility – a new tool to study plant–soil C cycling with a holistic approach. *Isotopes Environ. Health Stud.* **53,** 286–297 (2016).

68. R Core Team. R: A Language and Environment for Statistical Computing. (2015).

Supplement Manuscript 4

The wayward decomposition behaviour of Pyrogenic Carbon in soils

Moritz Reisser[1], Bernardo Maestrini[1,2], Maitane Iturrate-Garcia[3], Runi anak Sylvester Pungga[4], Samuel Abiven[1*]

1-Department of Geography, University of Zurich, Zurich, Zurich, Switzerland

2-Department of Forestry, Michigan State University, East Lansing, Michigan, USA

3-Department of Evolutionary Biology and Environmental Studies, University of Zurich, Zurich, Zurich, Switzerland

4-Forest Department of Sarawak, KM10, Jalan Datuk Amar Kalong Ningkan, 93250 Kuching, Sarawak, Malaysia

*Corresponding author: samuel.abiven@geo.uzh.ch

Part B – Manuscripts

	Input	Site-specific Treatment	Recovery of initial input [%] 0-3 cm		0-6 cm		6-10 cm		Bulk		fLF		oLF		HF	
Tropical (Borneo)	grass	normal	8.6	±1.1	1.7	±0.2	1.3	±0.2	**11.6**	**±1.2**	2.2	±0.7	0.5	±0.2	6	±0.9
		drought	11.3	±1	1.4	±0.2	1	±0.2	**13.6**	**±1**	5.2	±1.1	0.9	±0.3	5.2	±0.7
	char	normal	80	±5.1	0.8	±0.2	0.9	±0.4	**81.7**	**±5.3**	68.7	±6.6	3	±1	8.2	±1.7
		drought	85.1	±2.5	0.5	±0.1	0.2	±0.1	**85.9**	**±2.5**	70.7	±3.9	8	±3.8	6.4	±1
Temperate (Switzerland)	grass	high pH	13.2	±1.7	1.5	±0.8	0.9	±0.5	**15.6**	**±1.6**	3.6	±1.4	1.3	±0.5	8.2	±1.1
		low pH	12.8	±3.3	1.1	±0.3	1.5	±0.4	**15.4**	**±3.5**	2.9	±1.3	1.9	±0.5	8	±2.1
	char	high pH	56.7	±2.9	2.1	±0.9	0.3	±0.3	**59.1**	**±2.4**	33.4	±4.5	13.3	±2.5	10	±1.2
		low pH	57.6	±2.9	1	±0.2	0.8	±0.2	**59.4**	**±2.8**	30.9	±3.4	11.2	±2.4	15.6	±2.9
Arctic (Siberia)	grass	wet	32.5	±2.7	1.5	±0.2	0.4	±0.1	**34.4**	**±3**						
		dry	30.4	±3.4	1.9	±0.2	0.6	±0.1	**33**	**±3.6**						
	char	wet	83.5	±6.2	1.2	±0.3	0.3	±0.1	**85.1**	**±6.1**						
		dry	85.6	±6.6	1.4	±0.2	1.4	±1	**88.4**	**±6.5**						

Table S1: Mean recovery of initial input. Fraction recoveries were normalized on the first horizon since they were measured for the first horizon. No fractions are given in Siberia, as everything can be considered fLF

Table S2: Additional Site-Information

Site	Longitude	Latitude	MAT [°C]	MAP [mm]	pH [H2O]	Soil Type [WRB - FAO]	Clay Content [%]	Site-specific Treatment	SOC content [g kg-1]
Tropical (Borneo)	114°02’	4°12’	27	2740	4.2	Arenosol	13±2	Drought Normal	1.69±0.21
Temperate (Switzerland)	8°22’	47°29’	8.4	930	5.44 6.61	Cambisol Leptosol	31.5±1.4	Low pH High pH	4.86±0.33
Arctic (Siberia)	147°28’	70°49’	-13.1	232	5.84	histic Cryosol	n.a.	High water table Low water table	33.36±1.3

References:

Singh, N. *et al.* Transformation and stabilization of pyrogenic organic matter in a temperate forest field experiment. *Glob. Chang. Biol.* **20,** 1629–1642 (2014).

Kumagai, T. et al. Annual water balance and seasonality of evapotranspiration in a Bornean tropical rainforest. Agric. For. Meteorol. 128, 81–92 (2005).

An, S. T. et al. — Mini Review — Review of Soils on the 52 ha Long Term Ecological Research Plot in Mixed Dipterocarp Forest at Lambir , Sarawak , Malaysian Borneo. Tropics 18, 61–86 (2009).

Ruehr, N. K. & Buchmann, N. Soil respiration fluxes in a temperate mixed forest: Seasonality and temperature sensitivities differ among microbial and root-rhizosphere respiration. Tree Physiol. 30, 165–176 (2009).

Iturrate-Garcia, M. et al. Interactive effects between plant functional types and soil factors on tundra species diversity and community composition. Ecol. Evol. 6, 8126–8137 (2016).

Ohashi, M. et al. Characteristics of soil CO2 efflux variability in an aseasonal tropical rainforest in Borneo Island. Biogeochemistry 90, 275–289 (2008).

Part C – Appendix

Curriculum Vitae

Moritz Reisser

Address: Schumacherweg 9, 8046 Zurich

Contact: moritz.reisser@gmail.com, +41 78 879 63 59

Born: 2.5.1990, Lauf an der Pegnitz, Germany

Citizenship: Germany

Education

2015 – now	**Graduate School** in Geography/Earth System Science, University of Zürich
2012 – 2014	**Master of Science** in Earth System Science, University of Zurich, Master's thesis: "Soil analysis at Mount Etna to explain faster tree growth preceding a volcanic eruption"
2009 – 2012	**Bachelor of Science** in Earth Science, Swiss Federal Institute of Technology (ETH), Zurich
2005 – 2009	**Secondary Education**, Major in Spanish, Kantonsschule am Burggraben, St. Gallen

Practical Experience

2015 – now	**Research Assistant (PhD candidate)**, University Research Priority Program on Global Change and Biodiversity, University of Zurich
2014	**Technician**, Glaciology and Geomorphodynamics Group, Department of Geography, University of Zurich
2013	**Internship**, Surface Waters Group, EAWAG, Kastanienbaum, Lucern

Conference Contributions:

Reisser, M., Maestrini, B., Yamasaki, E., Abiven, S. (2017): Charcoal has a mind of its own – The decomposition patterns of charcoal and grass in a set of different ecosystems. Oral presentation, 6th International Symposium on Soil Organic Matter, Harpenden, United Kingdom.

Reisser, M., Purves, S. R., Schmidt, M. W. I., Abiven, S. (2016): The Fate of Fire-Derived Carbon in Soils - A Global Estimation of Concentrations and Stocks. Poster Presentation, URPP GCB (University Research Priority Program on Global Change and Biodiversity) Conference 2016, Monte Verità, Ascona, Switzerland.

Reisser, M., Abiven, S., Schmidt, M. W. I. (2016): Global Distribution of Pyrogenic Carbon. PICO presentation, EGU (European Geoscience Union) General Assembly 2016, Vienna, Austria.

Reisser, M., González-Domínguez, B. R., Hagedorn, Frank, Abiven, S. (2016): Pyrogenic Carbon in forest soils across climate and soil property gradients in Switzerland. PICO presentation, EGU (European Geoscience Union) General Assembly 2016, Vienna, Austria.

Additional Publications

Lüthi, Martin P; Vieli, Andreas; Moreau, Luc; Joughin, Ian; **Reisser, Moritz**; Small, David; Stober, Manfred (2016). A century of geometry and velocity evolution at Eqip Sermia, West Greenland. *Journal of Glaciology*, 62(234):640-654.

Hastings, Alexander K; **Reisser, Moritz**; Scheyer, Torsten M (2016). Character evolution and the origin of Caimaninae (Crocodylia) in the New World Tropics: new evidence from the Miocene of Panama and Venezuela. *Journal of Paleontology*, 90(02):317-332.

Coppola, A., Wiedemeier, D. B., Galy, V., Haghipour, N., Hanke, U., Nascimento, G. S., Usman, M., Blattmann, T. M., **Reisser, M**., Freymond, C. V., Zhao, M., Voss, B., Schefuss, E., Wacker, L., Peucker-Ehrenbrink, B., Abiven, S., Schmidt, W. I., Eglinton, T. I (2018). Global scale evidence for the refractory nature of river particulate black carbon. Accepted at: *Nature Geoscience*.

Friedli, C. N., **Reisser, M**., Studer, M., Hund, A. and S. Abiven. Carbon root-derived, rhizodeposition, induced priming effect and mineralization differ between two different winter wheat genotypes. *In preparation*.

Gmünder, L., **Reisser, M**., Abiven, S. Fragmentation of Charcoal. *In preparation*.

Acknowledgements

There are many people who deserve a lot of gratitude and acknowledgement for helping, guiding or supporting me through this work.

Firstly, I would like to thank all my colleagues and co-workers at University of Zurich and the places I have visited in the course of my project. These are (alphabetically): Alessandra Musso, Alysha Coppola, Beatriz de los Reyes González-Domínguez, Cordula Friedli, Cyrill Zosso, Daniel Wiedemeier, Emily Solly, Eri Yamasaki, Fanny Petibon, Francesca Calitri, Gabriela Schaepman-Strub, Gerald Raab, Guido Wiesenberg, Ivan Woodhatch, Jonas Rudin, Juliane Hirte, Kavita Srivastava, Lukas Gmünder, Max Boxleitner, Michael Hilf, Mirjam Studer, Nicholas Ofiti, Philippa Ascough, Raquel Portes, Richard Baxter, Sandy Röthlisberger, Sergey Asanayev and Ulrich Hanke. Thank you all!

Secondly, it is always important to share such times with office-mates, which go through similar situations and work stages. My thanks go to Benjamin Fischer, Rick Assendelft, Jana Erdbrügger and Martina Gocke, who all made me feel confortable on my desk and providing me with stories, Dutch lessons or “snoepjes / drop”.

I want to thank my committee Michael Schmidt, Ross Purves and Samuel Abiven, for supporting me and keeping track of my progress. Without the good planning in the beginning, it would not have been possible to achieve this thesis in the timeframe it was.

I also want to acknowledge the URPP GCB and all the people I could meet and share knowledge with because of it. It was firstly my funding institution but also fostered interdisciplinary collaboration, mutual motivation and networking. Furthermore, it provided the means to visit all the nice places I have been working at in the field.

Special thanks go to Christian Meyer, who was not only flatmate and great support over a most of the time of the project, but also spent a lot of time reading and correcting the synthesis of the thesis.

Then, I would also like to thank my family and friends and all the people around me, outside from University, supporting me, helping me and making me enjoy life besides the “job”.

Last but certainly not least I want to thank a certain S. Holmes[1]. His sharp mind and rational thinking helped not only conceive this whole project, but also analyse and interpret it “out of the box” and in freshly exciting ways[2]. It was impressive to see how often he would see the small but essential details, which form a good conclusion. I maybe have acquired a basic (or maybe only superficial) understanding of his deductive reasoning during my time here and it was a pleasure and honour to be the J. Watson[3] in this.

…And I must say that a game of tennis from time to time does definitely a good job in motivating people[4]. Merci!

[1] name changed

[2] I think it is important to point out at this place that the real person has no drug problem like the fictional character behind the name.

[3] obviously I will only be Dr. afterwards, but I think it is a fitting comparison

[4] ...and winning even more so!